SEP 12
1958

Physics

REGISTERED No. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY OF SCIENCES

VOL. XLVII] *SECTION A* [No. 6

JUNE 1958

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THE DIFFRACTION OF X-RAYS BY DIAMOND: PART II

By Sir C. V. Raman

(*Memoir No.* 109 *of the Raman Research Institute, Bangalore*-6)

Received May 5, 1958

1. Introduction

For various reasons, diamond is the ideal case for a consideration of the consequences following from the ideas set out in Part I of this series of papers regarding the diffraction of X-rays by crystals. Since diamond is a cubic crystal of relatively simple structure, it is possible to determine and describe in purely geometrical terms the modes of vibration of which that structure is capable and with which we are concerned. It can also be shown that these modes have a high frequency, from which again it follows that they would not be thermally excited to any appreciable extent at ordinary temperatures. For the same reason also, it is permissible to ignore the disturbing effects on the phenomena with which we are concerned, of the thermal agitation in the crystal. It accordingly becomes possible to present a very clear picture of the effects which may be expected to present themselves to observation in strongly exposed X-ray diffraction patterns of diamond, on the basis of the theory developed in Part I.

2. The Structure of Diamond

Diamond exhibits in its structure a complete justification of Van't Hoff's hypothesis of the tetrahedral carbon atom. That hypothesis was originally put forward on the basis of the known chemical behaviour of carbon. It implies that the four valences which carbon exhibits in its compounds are tetrahedrally disposed in space and are indistinguishable from each other. Why this is so is one of the fundamental problems of theoretical chemistry. According to the spectroscopist's view of atomic structure, the nucleus of the carbon atom is surrounded by six electrons, two of which are in the inner or K-shell and the other four in the outer or L-shell. The latter four electrons again are assigned to two sub-groups, each containing two electrons. In the first sub-group, the electrons are assumed to be in the $2s$ state, while the two electrons in the other sub-group are in the $2p$ state. This situation of the four outer electrons is not in agreement with that indicated by the facts

of chemistry and hence it becomes necessary to modify the description of their states to bring it into line with the known chemical behaviour of carbon. All the four electrons have indeed to be considered as being in states indistinguishable from each other and so orientated that the resulting structure has perfect tetrahedral symmetry. Such a concept is necessary also to fit the picture of the carbon atom into the known facts concerning the structure of diamond. Having only two atoms in each unit cell, diamond nevertheless exhibits cubic symmetry. This situation requires that the nuclei of the carbon atoms occupy certain special positions in the crystal structure, namely, the points at which the four trigonal axes of cubic symmetry intersect each other.

The theory of hybridised orbitals is one of the best known attempts in the direction of describing the electronic state of the carbon atom in such manner as to bring it into line with the hypothesis of Van't Hoff. As full accounts of that theory are to be found in several recent treatises, it is not necessary here to expound it in detail. It is sufficient to mention that the states of the four electrons are assumed in that theory to be representable as a superposition of four hydrogen-like wave-functions which are so chosen that all the four electrons appear in similar states differing only in their orientations, which again exhibit tetrahedral symmetry. In the wave-functions assumed for the purpose, the $2p$ states preponderate, and hence each of the four electrons is implicitly assumed to possess an orbital angular momentum about an axis which coincides in direction with its directed valence. We may remark that for the shell of valence electrons thus constituted to possess true tetrahedral symmetry, it is necessary that the orbital movements of the four electrons about their respective axes should be described in the same sense, that is to say, either all of them in a right-handed sense, or else all of them in a left-handed sense. We are thus led to recognize that there are two possible descriptions of the carbon atom, namely, a dextro-carbon atom and a lævo-carbon atom, which correspond respectively to the two possible senses of the orbital angular momentum of the electrons about the tetrahedral valence directions.

The considerations set forth above have important consequences in relation to the structure and physical properties of diamond. That crystal is usually described as made up of two non-equivalent sets of carbon atoms each located at the points of a face-centred cubic lattice; the two lattices interpenetrate each other in such manner that every carbon atom in one lattice is tetrahedrally surrounded by four others belonging to the other lattice. Accepting this description, it follows that in a truly homogeneous crystal of

diamond, only one out of four possible situations can exist: (i) both lattices are occupied by dextro-carbon atoms, (ii) both lattices are occupied by lævo carbon atoms, (iii) one lattice is occupied by dextro-carbon atoms and other by lævo-carbon atoms, or (iv) the first lattice is occupied by lævo- and the second by dextro-carbon atoms. It is entirely possible that two or three or all four of these possible structures may exist simultaneously in different parts of the same crystal. It is sufficient, however, to consider here only the case of truly homogeneous diamonds the structure of which is exclusively one or another of the four categories set out above.

3. The Vibration Spectrum of Diamond

The vibration spectrum of a crystal containing p atomic nuclei in each unit cell consists of $(24p - 3)$ distinct modes with monochromatic frequencies, supplemented by a continuous spectrum which is the residue representing the three omitted degrees of translatory freedom of motion. Since the unit cell of diamond contains 2 atomic nuclei only, we have 45 possible modes of vibration with monochromatic frequencies. The description of these modes and the evaluation of their frequencies have been very fully set out in an earlier memoir published in these *Proceedings*. In two other memoirs again, it has been shown that the heat capacity of diamond over the entire range of temperatures may be quantitatively evaluated in terms of these frequencies. It is therefore unnecessary to traverse the same field again, and indeed in the present paper we are only concerned with the three modes of vibration of highest frequency which may be described as an oscillation of the two lattices of carbon atoms with respect to each other along one or another of the three cubic axes. The free vibrations of the structure in all these three modes have the same frequency, and this is known exactly from spectroscopic studies on the diffusion of monochromatic light in diamond. A sharply defined line with a frequency shift of 1332 cm.$^{-1}$ is recorded in the spectrum of the scattered light, and this frequency is associated with a vibration of the kind described above.

Whether the mode of vibration referred to above would be excited by the passage of X-rays through the crystal depends, as we have seen in Part I, on whether this mode is or is not active in the absorption of infra-red radiation. The circumstances which determine whether a specified mode of vibration in a crystal is active or not in the absorption of infra-red radiation have been considered by various authors and will be found discussed in detail in several recent treatises. It is a well-established rule deduced from theory and confirmed experimentally that if a structure possesses centres of symmetry,

any mode of vibration which manifests itself as a frequency shift in light scattering would be *inactive* in the absorption of infra-red radiation. In the first two sub-species of diamond referred to above, both sets of carbon atoms are dextro-carbon atoms or both lævo-carbon atoms respectively. It is clear that every point midway between a pair of atoms belonging respectively to the two lattices would in these cases be a centre of symmetry. Accordingly, in these two sub-species of diamond, since the mode of vibration with the frequency 1332 cm.$^{-1}$ manifests itself as a frequency in light-scattering, that mode would be *inactive* in infra-red absorption. *Per contra*, in the two other sub-species of diamond where the carbon atoms located at the points of the two lattices are of different species, the points midway between two carbon atoms are *not* centres of symmetry. Hence the rule of mutual exclusion stated above is not applicable in their cases and hence the modes of vibration would be active *both* in the scattering of light and in the absorption of infra-red radiation. In what follows, we shall refer to the first two sub-species of diamond as the Oh I and Oh II types of diamond respectively, and the two other sub-species as Td I and Td II respectively. The use of these symbols has a special significance, *viz.*, that the electronic structure of the first two species of diamond has the full or octahedral symmetry of the cubic system, whereas the electronic structure of the two other species has only the lower or tetrahedral symmetry.

We may conclude this section by a categorical statement of the results indicated by the theory. *In diamonds which belong to the two sub-species Oh I and Oh II, the fundamental vibration of the structure with frequency of* 1332 *cm.*$^{-1}$ *would not be active in infra-red absorption and hence the passage of X-rays through the crystal would not excite that vibration and hence would not result in a dynamic reflection.* Per contra, *in diamonds which belong to the two other sub-species Td I and Td II, the said vibration would be active in the absorption of infra-red radiation and hence the passage of X-rays through the crystal would excite those vibrations and give rise to dynamic reflections by the lattice planes in the crystal.*

4. THE PHASE WAVES OF DYNAMIC REFLECTION

We shall proceed to consider the nature of the dynamic reflections which may be expected to manifest themselves in the case of diamonds possessing only the lower or tetrahedral symmetry of electronic structure as the result of the excitation of the infra-red active vibration. As already stated, this vibration is an oscillation of the interpenetrating lattices of carbon atoms (in these cases dissimilar to each other) along one or another of the three cubic axes of the crystal. The atoms belonging to the two lattices appear in distinct but

equidistant layers parallel to the cubic planes. The infra-red activity of the vibration arises from the fact that the electronic structure of the carbon atoms in the alternate layers is not completely identical. Hence, the oscillations of the two lattices with respect to each other results in periodic displacements of electric charge along the direction of vibration. We have three such movements to consider, which are respectively along one or another of the three cubic axes of the crystal. Hence, we have also three sets of phase-waves to consider whose normals are likewise the cubic axes.

The oscillatory movements of electric charge along the cubic axes of the crystal would necessarily also result in periodic movements of the stratifications of electric charge which appear in the crystal in other directions. In considering the question whether these movements would give rise to dynamic reflections by those stratifications, we have to remark that movements *parallel* to any set of stratifications cannot give rise to any dynamic reflections by them; only movements *normal* to the stratifications can give rise to such reflections, and hence if the actual movements are *inclined* to the stratifications, we need consider only the components of the movement along their normals.

Considering for example the (111) planes in a crystal, the three movements respectively along the three cubic axes are equally inclined to those planes, and hence the magnitude of all the three components resolved along the normal to the (111) planes would be diminished to the same extent. Hence, in general, *the* (111) *planes would give three dynamic reflections* which in appropriate circumstances, may be expected to be of comparable intensities. On the other hand, the (220) planes of the crystal contain one cubic axis and are equally inclined to the other two at angles of 45°. The displacements of electric charge parallel to the first axis and hence also parallel to the plane of the stratifications would not give rise to any dynamic reflection. However, movements along the two other cubic axes would result in a displacement of the stratifications in the (220) planes diminished to equal extents by reason of their inclination to those planes. We conclude that *the* (220) *planes would give only two dynamic reflections* which in appropriate circumstances would be of equal intensity. Considering again the (400) planes, these contain two of the cubic axes and are normal to the third, it follows for similar reasons that *the* (400) *planes give only one dynamic reflection.* The fact that the phase-waves are parallel to those planes has a further interesting consequence to which we shall revert later. Finally, we may briefly consider the (311) planes. These planes are equally inclined to two of the cubic axes at small angles and are nearly perpendicular to the third. The dynamic

reflections due to the first two movements may therefore be expected to behave very differently from the third.

5. THE GEOMETRY OF THE DYNAMIC REFLECTIONS

The general method already indicated in Part I enables us to picture the configuration of the dynamic reflections given by the various lattice planes in the crystal. We shall here content ourselves with the consideration of the dynamic reflections associated with the (111), (220), (311) and (400) planes, since these are the four largest spacings in the crystal which also reflect X-rays with notable intensity. The first three cases are represented in Figs. 1, 2 and 3 respectively for settings of the crystal so chosen that the

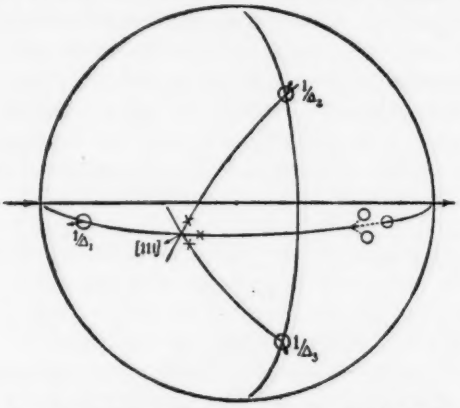

FIG. 1. Dynamic Reflections by the (111) planes.

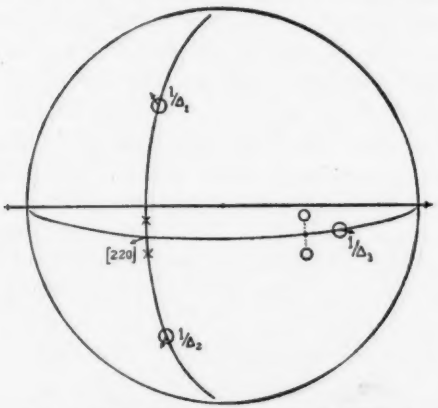

FIG. 2. Dynamic Reflections by the (220) planes.

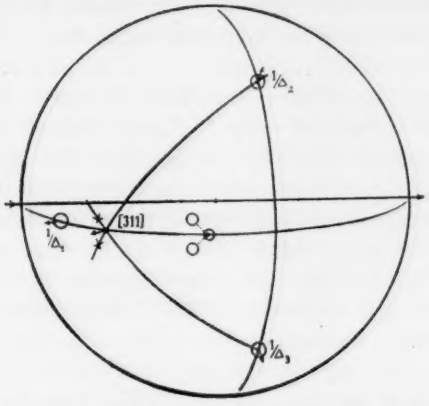

FIG. 3. Dynamic Reflections by the (311) planes.

characteristic features of each case are brought out clearly. The primary X-ray beam is assumed to traverse the crystal horizontally and its direction is indicated by arrows at the points of entry and exit on a sphere. The plane of incidence on the lattice-spacings is also assumed to be horizontal and is indicated by a great circle drawn on the surface of the sphere. The normal to the lattice spacings accordingly appears as a point on the same great circle with an arrow attached to it and directed radially outwards. The three cubic axes of the crystal which are the normals to the phase-waves of dynamic reflection are represented on the sphere in a similar fashion, the points where they appear being determined by the chosen setting of the crystal. Three great circles are also drawn each of which contains one of the phase-wave normals and the normal to the lattice spacings. In each case the setting of the crystal chosen is such that one of the great circles coincides with the plane of incidence. The normals to the three sets of dynamic stratifications would necessarily lie on these three great circles. The positions of the dynamic reflections would be determined by drawing three other great circles, each containing the direction of the incident beam and the normal to the particular dynamic stratification, and marking off on these circles, points such that the angle of reflection is equal to the angle of incidence in the respective planes. The entire procedure is that indicated by the theory of dynamic reflection developed in Part I and contained in the two equations

$$\frac{\vec{1}}{D} = \frac{\vec{1}}{d} + \frac{\vec{1}}{\Delta} \qquad (1)$$

$$2D \sin \psi = \lambda \qquad (2)$$

For a particular X-ray wavelength determined by the lattice spacings and the angle of incidence of the X-rays on them, we would observe the ordinary or unmodified reflection in the plane of incidence. The direction in which this appears is represented in each of the figures as another point on the equatorial circle. For the same X-ray wavelength, the dynamic reflection or reflections permitted would also appear in the same direction superposed on the ordinary or static reflection. For other X-ray wavelengths, the static reflection ceases to appear but the dynamic reflections would persist, their directions being determinable in the manner already explained. The phase wavelength is infinite for the particular case in which the static and dynamic reflections are superposed. With progressively changing X-ray wavelength, $1/\Delta$ would increase in numerical magnitude and the point on the sphere representing the dynamic stratification would move out in one direction or another along the great circle which defines its path. The construction already indicated would then result in giving positions to the dynamic reflections differing from that in which they were originally coincident. In the particular settings of the crystal which have been chosen for drawing the figures, the dynamic reflection which corresponds to the cubic axis in the plane of incidence would—if it exists at all—appear in the plane of incidence, while the other two would swing out of that plane symmetrically in either side.

For reasons already explained, whereas the (111) planes show *three* dynamic reflections in the setting indicated, the (220) planes show only two reflections: these are displaced laterally, one on either side. The third reflection lying in the plane of incidence though *geometrically* permitted is *physically* excluded by reason of the movement of the stratifications being in their own plane. The case of (400) reflection is of special interest. As explained earlier, only one dynamic reflection is possible in this case and since the phase-waves which give that reflection are parallel to the stratifications themselves, the dynamic reflection for all X-ray wavelengths would appear in the same direction, *viz.*, that indicated by the ordinary law of geometric reflection.

6. SUMMARY

Considerations of the physical nature of the directed valences of the tetrahedral carbon atom lead to the conclusion that there are two possible states of the carbon atom, *viz.*, a dextro-state and a lævo-state corresponding respectively to the two possible senses of the orbital angular momentum of the electrons about their tetrahedral valence directions. From this again it follows that a homogeneous diamond crystal may have an electronic structure which has either the highest or octahedral symmetry or else only the lower

or tetrahedral symmetry of the cubic system. In diamonds having octahedral symmetry, the oscillations of the two carbon atoms with respect to each other would be inactive in the absorption of infra-red radiation, whereas in diamonds of which the electronic configuration has tetrahedral symmetry that vibration would be active in such absorption. From this it follows that only with diamonds of the latter type would the X-rays excite the lattice vibrations and exhibit the dynamic reflections consequent thereon. The vibrations excited and their phase-wave-normals are parallel to the three cubic axes of the crystal. It follows that whereas the (111) planes would exhibit *three* dynamic reflections at any one setting of the crystal, the (220) would exhibit only *two* and the (400) planes only *one*.

STUDIES ON METALLIC HALIDE-DIOXANATES
PART I

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Received March 7, 1958

(Communicated by Dr. M. R. A. Rao, F.A.SC.)

A new method for the preparation of metallic chloride dioxianates is described. The method is very elegant and simple and appears to be of general application. In the present paper, isolation of mercuric chloride dioxanate by this new method is described.

Several workers have investigated the dioxane complexes of various metallic halides. Paterno and Spallino[1] reported first the existence of molecular compounds of dioxane with mercuric chloride. Crenshaw *et al.*[2] reinvestigated this and similar compounds of the mercuric halides. Dipole moment measurements of Curran and Wenzyke[3] and conclusions thereform supported the view that these compounds were dioxanates. Rheinboldt *et al.*[4] and Kelley and Mecusker[5] have studied many addition compounds of dioxane with the trihalides of arsenic, bismuth and antimony. The molecular compounds of dioxane with mercury cyanides and thiocyanates were described by Brand and Turck.[6]

The procedure adopted for the preparation of the complexes by these earlier workers, is the direct mixing of the metallic halide with dioxane. A new method for the preparation of hexachloroceric acid crystals from dioxane has been reported by Moosath and Rao.[7] The procedure adopted by these workers appears to be of general application in the isolation of metallic halide dioxanates and this technique has been extended in the case of mercuric chloride dioxane complex.

Experimental

Materials used

1. *Mercuric oxide.*—A. R. Grade mercuric acetate was dissolved in water and precipitated with a dilute solution of sodium hydroxide. The precipitate was allowed to stand for a few hours, filtered and washed free of soluble impurities. It was then dried at 110° C. for several hours, powdered and stored. Analysis of the sample showed it to be pure mercuric oxide.

2. *Dioxane.*—Technical quality dioxane was purified by the process recommended by Weisberger,[8] refluxed with sodium, distilled and stored with sodium wire.

3. Dry hydrogen chloride gas was prepared as and when required. Other reagents and chemicals used were of C.P. grade.

Analytical

The samples prepared were analysed for mercury and chlorine. Mercury was estimated gravimetrically by weighing as mercuric sulphide. Chloride estimations were carried out by the thiocyanate method in the filtrate obtained after removal of Hg as HgS and expulsion of hydrogen sulphide by boiling.

Preparation of mercuric chloride dioxanate.—Mercuric oxide (10 g.) was suspended in dioxane (200 ml.) and treated with dry dydrogen chloride gas. The contents of the reaction vessel were found to become hot rapidly and hence the vessel was cooled in tap water occasionally. Within about 30 minutes, the entire mercuric oxide dissolved. The solution was rapidly filtered out of contact with moisture and kept at 2° C. overnight when a solid phase appeared as white rhombic prisms. The crystals were filtered in a sintered funnel out of contact with moisture and cyrstallised from fresh dioxane. The crystals were transferred to a sintered funnel and dry air was passed continuously to remove any free dioxane till a constant dioxane composition was obtained. (Found: Hg, 55·9%, Cl, 19·9%. Calculated percentage for the formula $HgCl_2$–$C_4H_8O_2$, Hg, 55·8%, Cl, 19·75%.)

Crystals of the complex prepared as above were transferred to the sintered funnel and washed several times with pure dry petroleum ether which is miscible with dioxane in all proportions. Dry air was passed for a few minutes to remove the last traces of petroleum ether. Analytical results agreed with the formula $HgCl_2$–$C_4H_8O_2$.

A sample of the crystals recrystallised from dioxane was evacuated at 1 mm. pressure for 30 minutes and analysed. Molecular weight calculated from the percentage values of mercury as well as chloride yet agreed with the value calculated from formula $HgCl_2$–$C_4H_8O_2$.

Preparation of $HgCl_2$–$2\,C_4H_8O_2$.—As the initial results showed the possibility of the existence of a complex with more than one molecule of dioxane per molecule of mercuric chloride, the following experiment was carried out. The crystals prepared as above were dissolved in hot dioxane, filtered and the hot filtrate allowed to cool overnight. The crystals that had separated were transferred to the sintered funnel and dry air saturated with dioxane vapour at room temperature (28° C.) was passed through the funnel

containing the crystals. The partial pressure of dioxane in the current of air which is more than the dissociation pressure of the higher dioxanates would prevent any change to $HgCl_2$–$C_4H_8O_2$. When the crystals appeared to be solvent free, a sample was removed for analysis. (Found: Hg, 44·4%, Cl, 15·7%. Calculated for $HgCl_2$–2, $C_4H_8O_2$, Hg, 44·8%, Cl, 15·84%.) This treatment of the crystals for any length of time did not further change their composition.

Effect of crystallising the complex from other solvents

1. *Ethyl alcohol.*—The crystals prepared as above were dissolved in hot absolute alcohol, the solution filtered rapidly and allowed to cool overnight at 0° C. The white rod-shaped crystals that had collected were separated and freed from solvent by passing a current of dry air for one hour. The sample, on analysis, was found to contain Hg, 55·8%; Cl, 19·8%, agreeing with the values for the compound $HgCl_2$–$C_4H_8O_2$. To make sure that no alcohol which might have been present as a part of the complex was lost during the passage of air, another sample of the product crystallised from alcohol was dried in a current of dry air saturated with alcohol at room temperature. Analysis showed no change in composition proving the absence of any alcohol of solvation. Repeated crystallisation from alcohol also gave a product agreeing with the formula $HgCl_2$–$C_4H_8O_2$.

2. *From acetone.*—About 5 g. of the crystals $HgCl_2$—2 $C_4H_8O_2$ were dissolved in hot, anhydrous acetone. The clear solution was cooled to 0° C., and the complex got deposited as rod-shaped crystals. A part of the crystals was freed from the solvent by keeping in a current of air for one hour and another portion was dried in a current of dry air saturated with acetone at laboratory temperature. Both the samples on analysis gave identical values for percentages of mercury and chloride (Hg, 55·85%; Cl, 19·8%). These values agree very closely with the formula $HgCl_2$–$C_4H_8O_2$.

3. *From water.*—About 5 g. of the higher dioxanate were dissolved in a small quantity of (about 30 ml.) distilled water at 60° C. and allowed to cool overnight at 3° C., when long needle-shaped crystals separated. The crystals were separated and pressed several times between folds of filter-paper, to free from solvent. A sample of the product was then analysed as in previous cases. Values obtained were Hg, 50·8%; Cl, 18·1%; Calculated values for $HgCl_2$–$C_4H_8O_2$, 2 H_2O, Hg, 52·02%, Cl, 18–39%. A weighed quantity of the crystals was then kept in a desiccator containing phosphorous pentoxide for 12 hours and the loss in weight determined. The dehydrated product was analysed for mercury and the chloride. The values found were: Hg, 55·65%, Cl, 19·7%. Calculated values for $HgCl_2$–$C_4H_8O_2$, Hg, 55–8%

Cl, 19·75%. Calculated percentage of water in $HgCl_2$–$C_4H_8O_2$–2 H_2O = 9·01. Percentage of water lost over P_2O_5 (found) 8·92.

Discussion

Dioxane is found to co-ordinate with mercuric chloride to form two crystalline solids. The higher dioxanate $HgCl_2$–2 $C_4H_8O_2$ is stable only when in equilibrium with dioxane and is readily changed to the more stable $HgCl_2$–$C_4H_8O_2$. The higher dioxanates, on exposure to atmospheric air, slowly gives off dioxane changing finally to the lower dioxanate. This change can be accomplished rapidly by washing the sample with petroleum ether or crystallising from absolute alcohol or acetone.

The authors thank Dr. P. P. Pillay, Professor of Applied Chemistry, University of Kerala, for his valuable suggestions.

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THE CHARACTERISTIC ROOTS OF THE PRODUCT OF TWO MATRICES

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Received December 23, 1957

(Communicated by Dr. S. M. Shah, F.A.Sc.)

1. Introduction and Notations

Let A and B be two n-square matrices with elements in the field of complex numbers. In a recent paper[3] this author has proved certain results regarding the upper bounds of the characteristic roots, $c(AB)$, of the product matrix AB (i) in terms of the characteristic roots of A and B when both A and B are Hermitian and (ii) in terms of the characteristic roots of A, $(B + B^*)/2$ and $(B - B^*)/2\,i$ when A is Hermitian and B is any matrix.

In this paper, we find the upper and lower limits for the real and imaginary parts of $c(AB)$ in terms of the characteristic roots of the associated Hermitian matrices $(A + A^*)/2$, $(A - A^*)/2i$, $(B + B^*)/2$ and $(B - B^*)/2i$ when A and B are any complex matrices.

In what follows, let us set $H_1 = (A + A^*)/2$, $K_1 = (A - A^*)/2i$, $H_2 = (B + B^*)/2$ and $K_2 = (B - B^*)/2i$.

2. The Bound Theorems of Characteristic Roots

Theorem 1.—*Let A and B be two commuting* n*-square complex matrices, such that the Hermitian matrices* $(A + A^*)/2$, $(A - A^*)/2i$, $(B + B^*)/2$ *and* $(B - B^*)/2i$ *are at least positive semi-definite. Then*

$$c_m\left(\frac{A + A^*}{2}\right) c_m\left(\frac{B + B^*}{2}\right) - c_M\left(\frac{A - A^*}{2i}\right) c_M\left(\frac{B - B^*}{2i}\right)$$

$$\leq \mathrm{Re}\, c(AB) \leq c_M\left(\frac{A + A^*}{2}\right) c_M\left(\frac{B + B^*}{2}\right)$$

$$- c_m\left(\frac{A - A^*}{2i}\right) c_m\left(\frac{B - B^*}{2i}\right), \qquad (1)$$

and

$$c_m\left(\frac{A+A^*}{2}\right)c_m\left(\frac{B-B^*}{2i}\right)+c_m\left(\frac{A-A^*}{2i}\right)c_m\left(\frac{B+B^*}{2}\right)$$

$$\leq \mathrm{Im}\, c\,(AB) \leq c_M\left(\frac{A+A^*}{2}\right)c_M\left(\frac{B-B^*}{2i}\right)$$

$$+ c_M\left(\frac{A-A^*}{2i}\right)c_M\left(\frac{B+B^*}{2}\right), \tag{2}$$

where c_M *and* c_m *stand respectively for the greatest and least characteristic roots.*

Proof.—Every square matrix $A=(A+A^*)/2+(A-A^*)/2=H_1+iK_1$, where H_1 and K_1 are Hermitian matrices. Let the characteristic roots (necessarily real) of H_1 be $c_m(H_1)=\lambda_1\leq\lambda_2\leq\ldots.\leq\lambda_n=c_M(H_1)$. Then there exists a unitary matrix P such that

$$P^*H_1P=\text{diag.}\,(\lambda_1,\lambda_2,\ldots.,\lambda_n)\equiv D(\lambda),\ \text{say,}$$

whence

$$H_1=PD(\lambda)P^*. \tag{3}$$

Since the matrix K_1 is also Hermitian, there exists a unitary matrix Q, such that

$$Q^*K\,Q=\text{diag.}\ (\gamma_1,\gamma_2,\ldots.,\gamma_n)\equiv D(\gamma),\ \text{say, where}\ c_m(K_1)=\gamma_1\leq\gamma_2\leq\ldots.\leq\gamma_n=c_M(K_1)$$ are the (real) characteristic roots of K_1.

Therefore,

$$K_1=QD(\gamma)Q^*. \tag{4}$$

Equations (3) and (4) give

$$A=PD(\gamma)P^*+iQD(\gamma)Q^*. \tag{5}$$

Similarly, let $c_m(H_2)=\mu_1\leq\mu_2\leq\ldots.\leq\mu_n=c_M(H_2)$ be the (real) characteristic roots of H_2, $c_m(K_2)=\nu_1\leq\nu_2\leq\ldots.\leq\nu_n=c_M(K_2)$ be the roots of K_2, so that there exist unitary matrices R and S such that

$$B=RD(\mu)R^*+iSD(\nu)S^*, \tag{6}$$

where $D(\mu)\equiv\text{diag.}\,(\mu,\mu_2,\ldots.,\mu_n)$ and $D(\nu)\equiv\text{diag.}\,(\nu_1,\nu_2,\ldots.,\nu_n)$.

From (5) and (6) we have

$$AB=PD(\lambda)P^*RD(\mu)R^*-QD(\gamma)Q^*SD(\nu)S^*$$
$$+i\,[PD(\lambda)P^*SD(\nu)S^*+QD(\gamma)Q^*RD(\mu)R^*]. \tag{7}$$

and

$$A^*B^* = PD(\lambda)\,P^*RD(\mu)\,R^* - QD(\gamma)\,Q^*SD(\nu)\,S^* - i\,[PD(\lambda)\,P^*SD(\nu)\,S^* + QD(\gamma)\,Q^*RD(\mu)\,R^*]. \quad (8)$$

Now if σ is a characteristic root of AB, there exists a non-zero column vector $x = (x_1, x_2, \ldots, x_n)$, with complex co-ordinates, such that

$$\sigma x = ABx$$

or,

$$\sigma x^*x = x^*ABx, \quad (9)$$

Taking the conjugate transpose of both the sides of (9), we have

$$\bar{\sigma} x^*x = x^*(B^*A^*)\,x = x^*A^*B^*x, \quad (10)$$

since $AB = BA$ implies that $B^*A^* = A^*B^*$.

Adding (9) and (10), we have

$$(\sigma + \bar{\sigma})\,x^*x = x^*\,[AB + A^*B^*]\,x$$

or,

$$\left(\frac{\sigma + \bar{\sigma}}{2}\right) x^*x = x^*\,[PD(\lambda)\,P^*RD(\mu)\,R^*]\,x - x^*\,[QD(\gamma)\,Q^*\,SD(\nu)\,S^*]\,x. \quad (11)$$

By hypothesis, the Hermitian matrices H_1, K_1, H_2, K_2 are at least positive semi-definite (to be called p.s.d.), so that $\lambda_i \geq 0$, $\gamma_i \geq 0$, $\mu_i \geq 0$, $\nu_i \geq 0$ for $i = 1, 2, \ldots n$. Therefore the value of the first Hermitian form on the right-hand side of (11) at least does not decrease if we replace the diagonal matrices $D(\lambda)$ and $D(\mu)$ respectively by the scalar matrices $\lambda_n I$ and $\mu_n I$, and the value of the second Hermitian form at least does not increase if we replace the diagonal matrices $D(\gamma)$ and $D(\nu)$ respectively by the scalar matrices $\gamma_1 I$ and $\nu_1 I$. Thus we have

$$\left(\frac{\sigma + \bar{\sigma}}{2}\right) x^*x \leq \lambda_n\mu_n\,(x^*PP^*RR^*x) - \gamma_1\nu_1\,(x^*QQ^*SS^*x)$$

$$= (\lambda_n\mu_n - \gamma_1\nu_1)\,x^*x,$$

the matrices P, Q, R and S being unitary.

Since $x^*x > 0$, we obtain

$$\left(\frac{\sigma + \bar{\sigma}}{2}\right) \leq \lambda_n\mu_n - \gamma_1\nu_1,$$

or,

$$\mathrm{Re}\, c\,(\mathrm{AB}) \leq c_{\mathrm{M}}\,(\mathrm{H}_1)\, c_{\mathrm{M}}\,(\mathrm{H}_2) - c_m\,(\mathrm{K}_1)\, c_m\,(\mathrm{K}_2). \tag{12}$$

In order to find the lower bound for $(\sigma + \bar{\sigma})/2$ we observe that the value of the first Hermitian form on the right-hand side of (11) does not increase if we replace the diagonal matrices $\mathrm{D}(\lambda)$ and $\mathrm{D}(\mu)$ respectively by the scalar matrices $\lambda_1 \mathrm{I}$ and $\mu_1 \mathrm{I}$, and the value of the second Hermitian form on the right-hand side of (11) does not decrease if we replace the diagonal matrices $\mathrm{D}(\gamma)$ and $\mathrm{D}(\nu)$ respectively by the scalar matrices $\gamma_n \mathrm{I}$ and $\nu_n \mathrm{I}$. Thus we have

$$\left(\frac{\sigma + \bar{\sigma}}{2}\right) x^* x \geq \lambda_1 \mu_1\,(x^* \mathrm{PP}^* \mathrm{RR}^* x) - \gamma_n \nu_n\,(x^* \mathrm{QQ}^* \mathrm{SS}^* x)$$

$$= (\lambda_1 \mu_1 - \gamma_n \nu_n)\, x^* x.$$

Since $x^* x > 0$, we have

$$\left(\frac{\sigma + \bar{\sigma}}{2}\right) \geq \lambda_1 \mu_1 - \gamma_n \nu_n$$

or,

$$\mathrm{Re}\, c\,(\mathrm{AB}) \geq c_m\,(\mathrm{H}_1)\, c_m\,(\mathrm{H}_2) - c_{\mathrm{M}}\,(\mathrm{K}_1)\, c_{\mathrm{M}}\,(\mathrm{K}_2). \tag{13}$$

Combining (12) and (13), we obtain (1).

In order to prove (2), we subtract (10) from (9), and have

$$(\sigma - \bar{\sigma})\, x^* x = x^* [\mathrm{AB} - \mathrm{A}^* \mathrm{B}^*]\, x,$$

$$= 2ix^* [\mathrm{PD}(\lambda)\, \mathrm{P}^* \mathrm{SD}(\nu)\, \mathrm{S}^*]\, x + 2ix^* [\mathrm{QD}(\gamma)\, \mathrm{Q}^* \mathrm{RD}(\mu)\, \mathrm{R}^*]\, x$$

or,

$$\left(\frac{\sigma - \bar{\sigma}}{2i}\right) x^* x = x^* [\mathrm{PD}(\lambda)\, \mathrm{P}^* \mathrm{SD}(\nu)\, \mathrm{S}^*$$

$$+ \mathrm{QD}(\gamma)\, \mathrm{Q}^* \mathrm{RD}(\mu)\, \mathrm{R}^*]\, x. \tag{14}$$

By hypothesis, λ_i, γ_i, μ_i and ν_i for $i = 1, 2, \ldots, n$ are non-negative. Therefore the value of the Hermitian form on the right-hand side of (14) does not decrease if we replace the diagonal matrices $\mathrm{D}(\lambda)$, $\mathrm{D}(\nu)$, $\mathrm{D}(\gamma)$ and $\mathrm{D}(\mu)$ respectively by the scalar matrices $\lambda_n \mathrm{I}$, $\nu_n \mathrm{I}$, $\gamma_n \mathrm{I}$ and $\mu_n \mathrm{I}$, and we have

$$\frac{\sigma - \bar{\sigma}}{2i} \leq \lambda_n \nu_n + \gamma_n \mu_n, \text{ since } x^* x > 0,$$

or,

$$\mathrm{Im}\, c\,(\mathrm{AB}) \leq c_{\mathrm{M}}\,(\mathrm{H}_1)\, c_{\mathrm{M}}\,(\mathrm{K}_2) + c_{\mathrm{M}}\,(\mathrm{K}_1)\, c_{\mathrm{M}}\,(\mathrm{H}_2). \tag{15}$$

Similarly, we can prove that

$$Im\, c\,(AB) \geq c_m\,(H_1)\, c_m\,(K_2) + c_m\,(K_1)\, c_m\,(H_2). \tag{16}$$

Combining (15) and (16) we establish (2) and this completes the proof of the theorem.

If the matrices A and B of Theorem 1 are such that the Hermitian matrices H_1, K_1, H_2, K_2 are at least negative semi-definite (to be called n.s.d.), their characteristic roots are ≤ 0, so that in this case the above theorem takes the following form:

Theorem 2.—*Let A and B be two commuting* n*-square complex matrices, such that the Hermitian matrices* $(A - A^*)/2$, $(A - A^*)/2i$, $(B + B^*)/2$ *and* $(B - B^*)/2i$ *are at least negative semi-definite. Then*

$$c_M\left(\frac{A + A^*}{2}\right) c_M\left(\frac{B + B^*}{2}\right) - c_m\left(\frac{A - A^*}{2i}\right) c_m\left(\frac{B - B^*}{2i}\right)$$

$$\leq Re\, c\,(AB) \leq c_m\left(\frac{A + A^*}{2}\right) c_m\left(\frac{B + B^*}{2}\right)$$

$$- c_M\left(\frac{A - A^*}{2i}\right) c_M\left(\frac{B - B^*}{2i}\right), \tag{17}$$

and

$$c_M\left(\frac{A + A^*}{2}\right) c_M\left(\frac{B - B^*}{2i}\right) + c_M\left(\frac{A - A^*}{2i}\right) c_M\left(\frac{B + B^*}{2}\right)$$

$$\leq Im\, c\,(AB) \leq c_m\left(\frac{A + A^*}{2}\right) c_m\left(\frac{B - B^*}{2i}\right)$$

$$+ c_m\left(\frac{A - A^*}{2i}\right) c_m\left(\frac{B + B^*}{2}\right), \tag{18}$$

where c_M *and* c_m *denote respectively the greatest and least characteristic roots.*

We omit the proof of this theorem and consider the following:

THEOREM 3.—*Let A and B be two commuting* n*-square complex matrices such that* $(A + A^*)/2$ *and* $(A - A^*)/2i$ *are at least p.s.d., while* $(B + B^*)/2$ *and* $(B - B^*)/2i$ *are at least negative semi-definite. Then*

$$c_M\left(\frac{A+A^*}{2}\right)c_m\left(\frac{B+B^*}{2}\right)-c_m\left(\frac{A-A^*}{2i}\right)c_M\left(\frac{B-B^*}{2i}\right)$$

$$\leq \mathrm{Re}\, c\,(AB) \leq c_m\left(\frac{A-A^*}{2}\right)c_M\left(\frac{B+B^*}{2}\right)$$

$$-c_M\left(\frac{A-A^*}{2i}\right)c_m\left(\frac{B-B^*}{2i}\right), \tag{19}$$

and

$$c_M\left(\frac{A+A^*}{2}\right)c_m\left(\frac{B-B^*}{2i}\right)+c_M\left(\frac{A-A^*}{2i}\right)c_m\left(\frac{B+B^*}{2}\right)$$

$$\leq \mathrm{Im}\, c\,(AB) \leq c_m\left(\frac{A+A^*}{2}\right)c_M\left(\frac{B-B^*}{2i}\right)$$

$$+c_m\left(\frac{A-A^*}{2i}\right)c_M\left(\frac{B+B^*}{2}\right), \tag{20}$$

where c_M *and* c_m *denote respectively the greatest and least characteristic roots.*

Proof.—Since the Hermitian matrices H_1 and K_1 are at least p.s.d., $\lambda_i \geq 0$ and $\gamma_i \geq 0$ for $i = 1, 2, \ldots, n$; and since H_2 and K_2 are at least n.s.d., $\mu_i \leq 0$ and $\nu_i \leq 0$ for $i = 1, 2, \ldots, n$. Now, if we replace the diagonal matrices $D(\lambda)$, $D(\mu)$ $D(\gamma)$ and $D(\nu)$ in (11) respectively by the scalar matrices $\lambda_1 I$, $\mu_n I$, $\gamma_n I$ and $\nu_1 I$ the value of the Hermitian form on the right-hand side does not decrease. Hence, we have

$$\frac{\sigma+\bar{\sigma}}{2} \leq \lambda_1\mu_n - \gamma_n\nu_1,$$

or,

$$\mathrm{Re}\, c\,(AB) \leq c_m(H_1)\, c_M(H_2) - c_M(K_1)\, c_m(K_2). \tag{21}$$

Similarly, replacing the diagonal matrices $D(\lambda)$, $D(\mu)$, $D(\gamma)$ and $D(\nu)$ in (11) by $\lambda_n I$, $\mu_1 I$, $\gamma_1 I$ and $\nu_n I$ we can prove that

$$\frac{\sigma+\bar{\sigma}}{2} \geq \lambda_n\mu_1 - \gamma_1\nu_n,$$

or,

$$\mathrm{Re}\, c\,(AB) \geq c_M(H_1)\, c_m(H_2) - c_m(K_1)\, c_M(K_2). \tag{22}$$

Combining the inequalities (21) and (22), we establish (19).

Remembering the facts about the signs of the characteristic roots of the Hermitian matrices stated in the beginning of the proof of this theorem and replacing the diagonal matrices in (14) by suitable scalar matrices, we can likewise establish (20), and this completes the proof of Theorem 3.

So far we have considered only those matrices A and B for which the two pairs of the associated Hermitian matrices $(A + A^*)/2$, $(A - A^*)/2i$ and $(B + B^*)/2$, $(B - B^*)\,2i$ are p.s.d. or n.s.d., or one pair is p.s.d. the other being n.s.d. We now consider the following theorem in which one pair of the Hermitian matrices is indefinite, while the other is at least p.s.d.:

THEOREM 4.—*Let A and B be two commuting* n*-square complex matrices, such that* $(A + A^*)/2$, $(A - A^*)/2i$, *are indefinite, and* $(B + B^*)/2$, $(B - B^*)/2i$ *are at least positive semi-definite. Then*

$$c_m\left(\frac{A + A^*}{2}\right) c_M\left(\frac{B + B^*}{2}\right) - c_M\left(\frac{A - A^*}{2i}\right) c_M\left(\frac{B - B^*}{2i}\right)$$

$$\leq \mathrm{Re}\, c\,(AB) \leq c_M\left(\frac{A + A^*}{2}\right) c_M\left(\frac{B + B^*}{2}\right)$$

$$- c_m\left(\frac{A - A^*}{2i}\right) c_M\left(\frac{B - B^*}{2i}\right), \tag{23}$$

and

$$c_m\left(\frac{A + A^*}{2}\right) c_M\left(\frac{B - B^*}{2i}\right) + c_m\left(\frac{A - A^*}{2i}\right) c_M\left(\frac{B + B^*}{2}\right)$$

$$\leq \mathrm{Im}\, c\,(AB) \leq c_M\left(\frac{A + A^*}{2}\right) c_M\left(\frac{B - B^*}{2i}\right)$$

$$+ c_M\left(\frac{A - A^*}{2i}\right) c_M\left(\frac{B + B^*}{2}\right), \tag{24}$$

where c_M *and* c_m *denote respectively the greatest and least characteristic roots.*

The inequalities of this theorem can be established by replacing the diagonal matrices of (11) and (14) by suitable scalar matrices taking into account the facts that since H_1 and K_1 are indefinite, $\lambda_n > 0$, $\lambda_1 < 0$, $\gamma_n > 0$ and $\gamma_1 < 0$ and since H_2 and K_2 are at least p.s.d., their characteristic roots are non-negative.

Similar results may be proved when the Hermitian matrices H_2 and K_2 are at least p.s.d. and

either

(i) one of the two Hermitian matrices H_1 and K_1 is indefinite, the other being at least n.s.d.;

or

(ii) one of the Hermitian matrices H_1 and K_1 is at least n.s.d., the other being at least p.s.d.;

or

(iii) one of the Hermitian matrices H_1 and K_1 is at least n.s.d., the other being indefinite.

3. Some Special Cases of the Above Theorems

We now give certain examples to show that many interesting results can be obtained as particular cases of the above theorems.

(i) If we put $B = I$ in the above theorems, we have

$$c_m\left(\frac{A + A^*}{2}\right) \leq Re\, c(A) \leq c_M\left(\frac{A + A^*}{2}\right), \tag{26}$$

and

$$c_m\left(\frac{A - A^*}{2i}\right) \leq Im\, c(A) \leq c_M\left(\frac{A - A^*}{2i}\right), \tag{27}$$

results due to Hirsch[2] and Bromwich.[1]

(ii) If the two Hermitian matrices A and B commute and are at least p.s.d., then AB is also Hermitian so that all $c(AB)$ are real and non-negative. The limits for $c(AB)$ will, then, be given by

$$c_m(A)\, c_m(B) \leq c(AB) \leq c_M(A)\, c_M(B).$$

(iii) If A is skew-Hermitian, then $A + A^* = 0$. If, moreover, A is such that the Hermitian matrix $(A - A^*)/2i = -iA$ is at least p.s.d., then every $c(-iA)$ is real and ≥ 0, so that $c(iA) \leq 0$. Also, $c_m(-iA) = -c_M(iA)$, $c_M(-iA) = -c_m(iA)$. Similar relations hold for B if it is skew-Hermitian and $(B - B^*)/2i$ is at least p.s.d., so that $c(-AB)$ are real

and ≥ 0 and $c(AB) \leq 0$. For the commuting skew-Hermitian matrices A and B defined above, (1) reduces to

$$-c_M(-iA)\,c_M(-iB) \leq c(AB) \leq -c_m(-iA)\,c_m(-iB)$$

or,

$$-c_m(iA)\,c_m(iB) \leq c(AB) \leq -c_M(iA)\,c_M(iB)$$

or,

$$c_M(iA)\,c_M(iB) \leq c(-AB) \leq c_m(iA)\,c_m(iB).$$

Finally, I am thankful to Professor S. M. Shah for his help in the preparation of this paper.

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THE DIPOLE MOMENTS AND MOLECULAR STRUCTURE OF FORMYL AND ACETYL COMPOUNDS

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Received March 28, 1958

(Communicated by Prof. K. R. Krishnaswami, F.A.SC.)

Introduction

During the past two decades the concept of hyperconjugation has been employed to interpret and to correlate a variety of experimental facts.[4, 5] Since this was explicitly achieved by Baker and Nathan[1] to explain the anomalous behaviour of certain series of alkyl substituted compounds, this phenomenon has been subjected to a quantitative study by the method of molecular orbitals[20] and also by means of study of its effects on properties like bond length, heats of hydrogenation and dipole moment. Dipole moment studies have given characteristic evidence of hyperconjugation in aldehydes and nitriles,[16] chloroform and methyl chloroform,[17] acrylonitrile and isocrotyl chloride[13] and some unsaturated aldehydes, ethers, and halogen compounds.[23] Since this problem has not been adequately considered from the point of view of dipole moments a study of the electric moments of a series of compounds has been carried out with a view to investigate the extent of hyperconjugation in these compounds. Particular compounds for which dielectric measurements have been made are the following: Formhydrazide, Acethydrazide, Acetaldoxime, Acetoxime and Formamidoxime.

Experimental

Materials

Dioxan.—Dioxan which was the solvent employed in this work was purified by Eigenberger's method[11] the details of which are given in an earlier paper.[28] $d_{35°C.} = 1{\cdot}01690$, $\epsilon_{35°C.} = 2{\cdot}1890$.

Form and Acethydrazides.—The two hydrazides are prepared according to the method of Schöfer and Schwan.[24] Formhydrazide forms colourless deliquescent crystals, m.p. 54° C. and acethydrazide, colourless deliquescent crystals, m.p. 68° C.

Acetaldoxime.—The compound was obtained by the method of Dunstan and Dymond[7] by mixing equimolecular amounts of acetaldehyde-ammonia and hydroxylamine-hydrochloride. The oil was extracted with ether and purified by successive fractional distillation. b.p. 110–12° C.

Acetoxime.—This was obtained by the interaction of hydroxylamine and acetone.[31] The product was recrystallised thrice from petroleum ether. Colourless crystals, m.p. 60° C.

TABLE I

Temperature 35° ± 0·01° *C.*

Mole fraction	Dielectric constant	Density
	Formhydrazide	
0·003379	2·24450	1·01626
0·011525	2·32747	1·01758
0·003961	2·25850	1·01641
0·005174	2·26749	1·01658
	Acethydrazide	
0·004120	2·24830	1·01745
0·007783	2·29955	1·01785
0·012799	2·36500	1·01834
0·018697	2·44187	1·01894
	Acetaldoxime	
0·007644	2·22056	1·01792
0·038692	2·24053	1·01634
0·068421	2·25850	1·01484
0·078329	2·26450	1·01434
	Acetoxime	
0·008417	2·20613	1·01795
0·017370	2·21437	1·01711
0·024356	2·22021	1·01644
0·030981	2·22605	1·01584
0·036934	2·22811	1·01534
	Formamidoxime	
0·002678	2·20712	1·01794
0·004989	2·22260	1·01835
0·009263	2·51470	1·01911
0·008225	2·24253	1·01892

Formamidoxime.—The procedure of Nef[21] was employed for getting the substance by the interaction of potassium cyanide and hydroxylamine-hydrochloride. The final part of the experiment was modified so as to effect fractional crystallisation of formamidoxime from potassium chloride. The product was thrice recrystallised from ethyl acetate, m.p. 114° C.

Apparatus and methods of measurement

Measurements of dielectric constants were made using an A.C. mains-operated heterodyne-beat apparatus, complete details of which are given in an earlier paper.[28] Densities of the solutions were obtained using an Ostwald-Sprengel pycnometer with closed ground in caps at both ends. The molar refraction was calculated by the additivity method of bond refractions of Denbigh.[6] Atomic polarisation was neglected and the polarisation of the solute at infinite dilution was obtained using the mean values of the Hedestrand constants α and β.[14]

Discussion

A calculation of the dipole moments of the two hydrazides, *i.e.*, formhydrazide and acethydrazide and of the two oximes acetaldoxime and acetoxime for comparison with the observed values must necessarily involve prior knowledge of the geometrical structure of the basic hydrazide and oxime molecules. The available X-ray data enable us to assign definite bond angles for the two hydrazides and the oximes. Thus for the oximes the bond angles were taken from the X-ray data for acetoxime[2] and for the hydrazides the angles were derived from the X-ray work on hydrazine[12] and from the data on crystalline amides. The structures with bond angles used in the calculations are given below in Fig. 1.

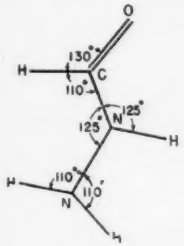

Fig. 1 A

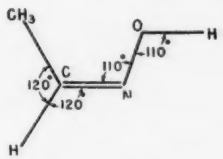

Fig. 1 B

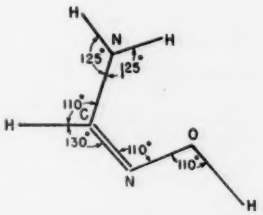

Fig. 1 C

Hydrazides and Oximes.—The expected resultant electric moments can be calculated from the characteristic bond moments tabulated by Smith.[26] The C = N moment was taken as 1·5 from the work of Everard and Sutton

on aldimines.[11] The calculations for the two hydrazide structures according as the NH_2 of the hydrazide group is on the right of the C—N axis or left yielded values 2·63 and 3·3 D respectively by the vector addition of bond moments, thereby indicating the former structure is more probable. Recently a method of evaluating the modification of bond moments due to induction along the polarisable bonds have been developed by Smith, Ree, Magee and Eyring[27] and this has been applied to the above-mentioned molecules (Fig. 2). In applying this treatment to the formhydrazide molecule, values of $\gamma_{C=O} = -2{\cdot}32$, γ_{X-C} (where $X = NH{\cdot}NH_2$) $= 1{\cdot}44$, derived from the dipole moments of formaldehyde[16] and methyl hydrazine respectively[30] were used, values of the other parameters being $\gamma_{HC} = 0$, $\beta_{HC} = 0{\cdot}13$, β_{XC} (where $X = NH{\cdot}NH_2$) $= 0{\cdot}243$, $\beta_{CO} = 0{\cdot}45$. Thus a value of 2·3 D was obtained. The higher experimental value should be considered to be due to the solvent effect. The difference between formhydrazide and acethydrazide moments, *i.e.*, 0·45 D can be ascribed to hyperconjugation.

For acetaldoxime, vector addition gives a moment of 0·77 D very close to the experimental value (0·75). For acetoxime the charges on each atom or group have been calculated by applying the method of Smith, Ree, Magee and Eyring. Application of this procedure using values of parameters γ_{C-X} (where $X = NOH$) $= 0{\cdot}731$, $\gamma_{C-H} = 0$, $\beta_{HC} = 0{\cdot}13$, β_{C-X} (where $X = NOH$) $= 0{\cdot}529$, derived from the dipole moment of acetaldoxime (0·75 D), $\gamma_{HC} = 0$ yielded a moment of 0·73 D, whereas the value obtained experimentally was 0·881 D (Table II). The higher value obtained over that calculated can be explained as due to hyperconjugation as in the case of acetaldehyde and acetone.

TABLE II

	Form-hydrazide	Acet-hydrazide	Form-amidoxime	Acet-aldoxime	Acet-oxime
Hedestrand α ..	4·505	6·119	3·147	0·278	0·4123
Hedestrand β ..	0·1529	0·0999	0·1747	−0·0502	−0·0891
Molar refraction ($cm.^3$)* ..	13·74	18·38	14·41	15·84	20·46
Total polarisation ($cm.^3$) ..	159·34	216·60	114·44	27·02	36·01
Orientation polarisation ($cm.^3$) ..	145·60	198·22	100·03	11·18	15·55
Dipole moment (D)	2·696	3·145	2·240	0·746	0·881

* Calculated from the bond refractions of Denbigh.[6]

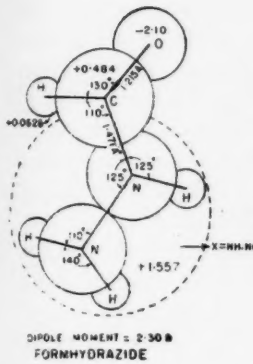

FIG. 2 A

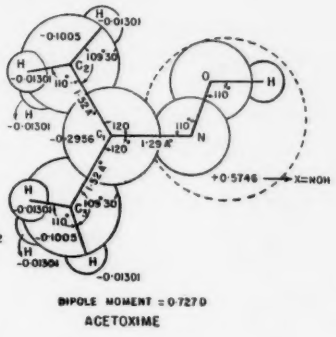

FIG. 2 B

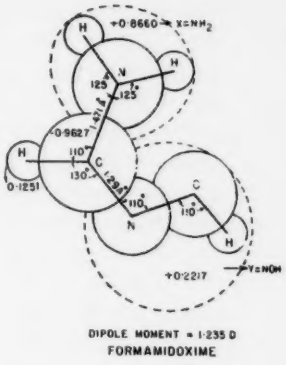

FIG. 2 C

Formamidoxime.—Discovered by Lossen and Schifferdecker in 1873[19] formamidoxime was recognised as a true amidoxime, isomeric with urea. The reactions and general properties of the amidoximes are best accounted for by the amidoxime structure. They form salts with alkalies like the oximes and do not reduce Fehlings solution. The numerous ring closure reactions which these compounds undergo give further evidence for the amidoxime structure. Geometrical isomerism would not be expected to occur in amidoximes themselves or in their substitution products of the type R—C (NHR) NOH because tautomerism with the form R—C (NR)—NHOH will allow interconverstion of the two stereoisomers. However, a search by Brady and Peakin[3] for stereoisomers by blocking tautomerism in NN′ disubstituted amidoximes, have proved unsuccessful. This has been explained as due to the assumption that the amidoximes have a betaine-like structure because attempts to methylate the hydroxyl group in these compounds failed. Further attempts to substantiate this assumption have, however, proved inconclusive.

Formamidoxime besides forming addition compounds with oxalic acid, sulphuric acid, etc., forms chelate complexes with copper, lead and iron ions. Since only the structure with the configuration —N—C can form the complex

$$\begin{array}{l} | \quad \| \\ \quad NOH \end{array}$$

as in the case of α benzil monoxime with the grouping C—C, the evidence

$$\begin{array}{l} \| \quad \| \\ O \ NOH \end{array}$$

is in favour of an oxime structure. Inner salt formation giving rise to a betaine-like structure is unlikely because betaines exhibit mesoionic character,[9] which is revealed only by the large dipole moment as in the case of Sydnones.[8]

The observed moment of formamidoxime is 2·24 D which rules out the possibility of a betaine-like structure for this compound. It will be proper to compare this compound with amides since this can be considered as an amide derivative. Richards and Thompson[22] point out on the basis of infrared measurements that in dilute solution in dioxan the amides exist predominantly in the keto form and this is supported by recent X-ray measurements on crystalline amides.[25] Therefore by considering only this keto form one can readily calculate the total moment by the vector addition of the component bond moments, once the geometry of the basic formamidoxime molecule is known. Because of strong evidence that the hydrogen atoms of the amino group do indeed lie in or very close to the plane of the amide group, moment calculations have been made assuming the valency angles as given in Fig. 1 C. The N—C=N and the C—N—H angles were taken from the X-ray data for dicyandiamide[15] and acetamide whereas the rest of the angles were from the X-ray work on acetoxime. Vector addition using the characteristic bond moments and a value of 1·5 D for the C = N bond, yields different values for different configurations of formamidoxime according to the disposition of the NOH group, of which more than one corresponds to a value nearer the experimental value. However, the moments induced in various parts of the molecule have also been calculated (Fig. 2 C) following Smith, Ree, Magee and Eyring. In applying this treatment to the formamidoxime molecule values of γ_{CX} (where X = NH_2) = 1·1, γ_{C-Y} (where Y = NOH) = 0·731 derived from the dipole moments of methyl amine[18] and acetaldoxime respectively, β_{XC} (where X = NH_2) = 0·243, β_{YC} (where Y = NOH) = 0·529, $\gamma_{HC} = 0$ and $\beta_{HC} = 0·13$ have been employed. The observed moment of 2·24 D for this compound differs from the calculated value (*i.e.*, 1·23 D) using the above method by 1·01 D. The higher moment of 2·24 D obtained experimentally can be ascribed to the effect of dioxan. This type of solvent solute interaction is not unlikely, *e.g.*, for oxypyridine,[29] the moment in dioxan is greater than that in benzene by 1·6 D.

SUMMARY

Dipole moment measurements have been made for the following formyl and acetyl derivatives, namely, formhydrazide, acethydrazide, acetaldoxime, acetoxime and formamidoxime in dioxan solution. The values obtained are 2·70, 3·15, 0·75, 0·88 and 2·24 (all in Debye units) respectively. The structure of the first four compounds have been discussed with particular reference to hyperconjugation. In the case of formamidoxime the results lead to an amidoxime structure.

ACKNOWLEDGEMENT

The authors wish to record their deep sense of gratitude to Prof. K. R. Krishnaswami, for his keen interest and valuable guidance during the course of this investigation.

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A NOTE ON CHARGE INDEPENDENCE AND NUCLEON-ANTINUCLEON INTERACTIONS

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Received March 1, 1958

(Communicated by Dr. Alladi Ramakrishnan, F.A.SC.)

1. Introduction

Since the advent of high energy accelerators, considerable data has been obtained on the following type of interactions:

$$N_1 + N_2 \rightarrow N_3 + N_4 + \pi \quad (1)$$

$$N_1 + \pi_1 \rightarrow N_2 + \pi_2 \quad (2)$$

where N_1, N_2, ... stand for nucleons and π, π_1, ... for charged and neutral π-mesons. More recently anti-nucleons have been produced in the laboratory (Segrè *et al.*, 1956).

It is unlikely that any consistent field theoretical calculation could be made at present with any chance of explaining the above reactions. Reaction (2) has been understood for low energies by the application of Chew's static theory. Nucleon-nucleon collision has not been studied except at threshold while nucleon antinucleon interaction has not yet received detailed attention. In view of the recent experiments on antinucleon production and also of Segré's experiments (1956) on proton antiproton scattering, it is considered worthwhile to draw some inferences on nucleon-antinucleon interactions on the basis of charge independence of nuclear forces.

2. Wave Functions in Isotopic Spin Space

The antiparticles can be brought into the present framework of isotopic spin if we adopt the Gellman-Nishijima assignment (Gellman, 1953; Nakano and Nishijima, 1953) of isotopic spin. According to this scheme, the particle and antiparticle have opposite values of T_3 the z-component of isotopic spin T. At first sight it might appear that it is not possible to distinguish between two systems one of which consists of a particle and an antiparticle and the other, of two particles. However the introduction of B the baryon number

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and the consequent definition of Q (the total charge of the system in units of e) by

$$Q = \sum_i (T_{3i} + \tfrac{1}{2} B_i) \tag{3}$$

makes it trivial since, for the first system $B = 0$ while for the second $B = 2$. We shall confine ourselves to the case $B = 0$.

Since the nucleon-antinucleon system is a strongly interacting one, the total isotopic spin T as well as M_T the z-component of T have to be conserved in addition to the conservation of baryon number. We shall use the abbreviation $a_{T,\,MT}$ to denote the wave function of total isotopic spin T and z-component M_T. The dependence on B (in the present case $B = 0$) is implicit. We next observe that the isotopic spins of a group of particles can be added in exactly the same way as the addition of angular momenta (see Blatt and Weisskopf, 1954). Thus we have

$$\begin{aligned}
a_{1,\,-1}(N\bar{N}) &= \bar{p}(1)\, n(2) \\
a_{1,\,0}(N\bar{N}) &= \frac{1}{\sqrt{2}}\{\bar{p}(1)\, p(2) + \bar{n}(1)\, n(2)\} \\
a_{1,\,1}(N\bar{N}) &= p(1)\, \bar{n}(2) \\
a_{0,\,0}(N\bar{N}) &= \frac{1}{\sqrt{2}}\{\bar{p}(1)\, p(2) - \bar{n}(1)\, n(2)\}
\end{aligned} \tag{4}$$

where p and n denote the isotopic spin wave functions for the proton and the neutron respectively and a bar over any particle denotes the corresponding antiparticle.

Next we re-express the nucleon and antinucleon wave functions in the isotopic spin representation. This is done by inverting the set of equations (4):

$$\begin{aligned}
\bar{p}(1)\, n(2) &= a_{1,\,-1} \\
p(1)\, \bar{n}(2) &= a_{1,\,1} \\
\bar{p}(1)\, p(2) &= \frac{(a_{0,\,0} + a_{1,\,0})}{\sqrt{2}} \\
\bar{n}(1)\, n(2) &= \frac{(a_{1,\,0} - a_{0,\,0})}{\sqrt{2}}
\end{aligned} \tag{5}$$

Using the set of equations (5) we can deal with all types of interactions.

3. Nucleon Antinucleon Scattering

From (5) it is obvious that the scattering amplitude for each of the processes

$$\bar{p} + n \rightarrow \bar{p} + n \tag{6}$$

$$p + \bar{n} \rightarrow p + \bar{n} \tag{7}$$

is $b\,(1)$, the reaction amplitude corresponding to T = 1.† To study the more interesting processes,

$$p + \bar{p} \rightarrow p + \bar{p} \tag{8}$$

$$p + \bar{p} \rightarrow n + \bar{n} \tag{9}$$

we analyse the incident wave function $\bar{p}p$ in terms of isotopic spins 1 and 0 as exhibited in equation (5) and re-express the isotopic spin amplitudes in terms of observable particles. Thus we arrive at the following results for direct and charge exchange scattering:

$$\text{ampl.}\,(\bar{p}p \rightarrow \bar{p}p) = \tfrac{1}{2}\{b\,(1) + b\,(0)\} \tag{10}$$

$$\text{ampl.}\,(\bar{p}p \rightarrow \bar{n}n) = \tfrac{1}{2}\{b\,(1) - b\,(0)\} \tag{11}$$

Hence the ratio of the scattering cross-sections is given by

$$\frac{\sigma\,(\bar{p}p \rightarrow \bar{p}p)}{\sigma\,(\bar{p}p \rightarrow \bar{n}n)} = \left(\frac{1+\alpha}{1-\alpha}\right)^2 \tag{12}$$

where α is the ratio $b\,(0)/\,b\,(1)$. Thus an experimental determination of the ratio of direct to charge exchange scattering fixes the value of α.

4. Production of Mesons in Nucleon-Antinucleon Annihilation

We shall confine ourselves to the production of mesons in proton antiproton annihilation since this can be more easily observed. Now we need the wave functions in isotopic spin space in terms of meson charge states. The wave functions corresponding to (1, 0) and (0, 0) states are given by

† We shall denote the reaction amplitudes corresponding to T = 1 and T = 0 by $b\,(1)$ and $b\,(0)$ respectively.

$$a_{1,0}(\pi\pi) = \frac{1}{\sqrt{2}}\{\pi^+(1)\pi^-(2) - \pi^-(1)\pi^+(2)\}$$

$$a_{0,0}(\pi\pi) = \frac{1}{\sqrt{3}}\{\pi^+(1)\pi^-(2) + \pi^-(1)\pi^+(2) - \pi^0(1)\pi^0(2)\} \quad (13)$$

These equations are obtained by the use of vector addition coefficients. The final state of the mesons produced by the annihilation of $\bar{p}p$ is

$$\frac{1}{\sqrt{2}}\{b(0)\,a_{0,0} + b(1)\,a_{1,0}\}$$

$$= \left\{\frac{b(0)}{\sqrt{6}} + \frac{b(1)}{2}\right\}\pi^+(1)\pi^-(2) + \left\{\frac{b(0)}{\sqrt{6}} - \frac{b(1)}{2}\right\}$$

$$\times \pi^-(1)\pi^+(2) - \frac{b(0)}{\sqrt{6}}\pi^0(1)\pi^0(2) \quad (14)$$

Thus we obtain the following result for charged and neutral production:

$$\sigma = \sigma(\pi^+\pi^-)\left\{\frac{[b(1)]^2}{2} + \frac{[b(0)]^2}{3}\right\} + \sigma(\pi^0\pi^0)\frac{[b(0)]^2}{6} \quad (15)$$

The ratio of charged to neutral production is therefore

$$2 + \frac{3}{\alpha^2}.$$

If α is determined from scattering experiments, this result serves as a test for the hypothesis of charge independence. From (15) it follows that if $T = 1$ state predominates, charged production predominates while prodominance of $T = 0$ state leads to charged and neutral production equally.

The results of this paper were obtained while the author was a Government of India Senior Scholar at the Department of Physics, University of Madras, and he would like to take this opportunity to express his indebtedness to Dr. Alladi Ramakrishnan for stimulating lectures and discussions during the summer of 1957 but for which the present work could not have been completed.

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POLYCYCLIC HYDROCARBONS

Part I. 3-Methyl-4, 5, 6, 6a-tetrahydro-6, 7-aceperinaphthanone-4

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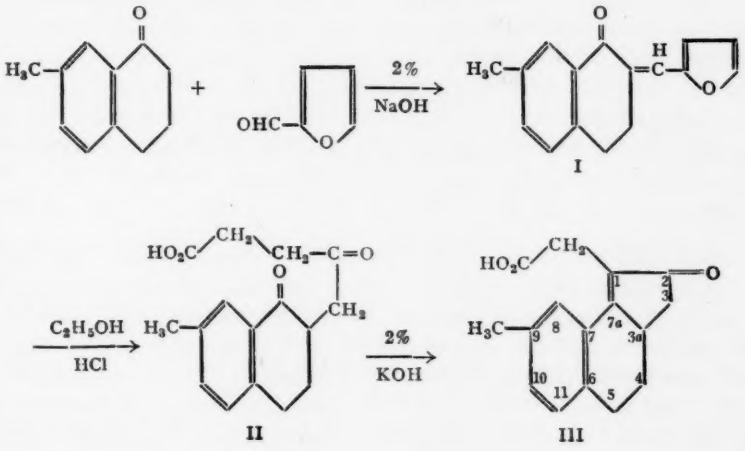
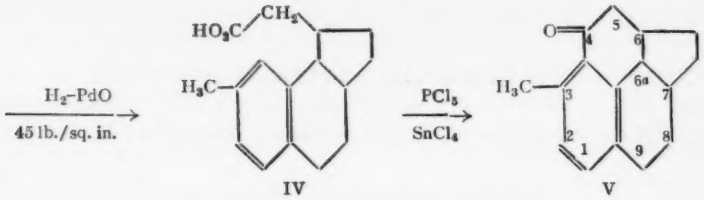
Received April 7, 1958

(Communicated by Dr. K. N. Menon, F.A.SC.)

THE cancer producing action of many polycyclic hydrocarbons has attracted much attention. Steranthrene, a new polycyclic hydrocarbon synthesised by Dannenberg,[1] was reported to produce tumours in mice. This hydrocarbon is characterised by the presence of aceperinaphthene ring system. Interest in derivatives of acenaphthene is evidenced in the synthesis of DL-beta (5-acenaphthenyl) alanine reported recently.[2] In the present work the synthesis of a methyl analogue of an aceperinaphthanone is reported.

7-Methyl-2-furfurylidene-α-tetralone (I) was prepared by condensing furfuraldehyde with 7-methyl-α-tetralone according to the method of Robinson,[3] and the project completed as shown by the following route which is essentially the same as employed by Dannenberg.[4]





The keto-valeric acid (II), obtained by the hydrolysis of furfurylidene tetralone (I), was subjected to intramolecular condensation with aqueous alkali to yield 9-methyl-3, 3*a*, 4, 5-tetrahydro-6, 7-benzindenone-2-acetic acid-1 (III). On catalytic hydrogenation with palladium oxide, III gave an oily acid, 9-methyl-tetrahydro-6, 7-benzindane acetic acid-1 (IV). This was cyclized to 3-methyl-4, 5, 6, 6 *a*-tetrahydro-6, 7-aceperinaphthanone-4. This compound can be employed to introduce other rings by taking advantage of the keto function. This requires accumulation of material which is engaging attention.

EXPERIMENTAL

7-Methyl-α-tetralone.—This was prepared by Barnett and Sanders[5] by the cyclisation of *γ-p*-tolyl-butyric acid employing sulphuric acid. It was found more profitable to prepare the tetralone by aluminium chloride cyclisation.[6] The crude ketone, from 33 g. of the acid, was purified by distillation under reduced pressure. b.p. 131–32°/9 mm., m.p. 35°. Yield 22 g.

7-Methyl-2-furfurylidene-α-tetralone (*I*).—Aqueous sodium hydroxide (2 ml. 8%) was added to a solution of freshly distilled furfuraldehyde (12 g.) and 7-methyl-α-tetralone (18 g.) in ethanol (50 ml.). The liquid immediately darkened and, after an hour, deposited a voluminous mass of pale yellow prisms. After 12 hours the crystals were collected and washed with ethanol. The product (22 g.) had m.p. 84°, unaltered by recrystallisation. A further quantity (1·5 g.) was obtained by diluting the mother liquor with water. The substance crystallised from alcohol in prisms. (Found: C, 80·3, H, 6·2. Theory: C, 80·3, H, 6·3.)

δ-[2-(7-Methyl-α-tetralone)]-γ-keto-valeric acid (*II*).—7-Methyl-2-furfurylidene-α-tetralone (18 g.) in ethanol (170 ml.) containing concentrated hydrochloric acid (40 ml.) was refluxed for 16 hours. The solvent was removed under reduced pressure and the dark brown tarry residue was boiled with a mixture of concentrated hydrochloric acid (50 ml.), acetic acid (50 ml.) and water (100 ml.) for 3 hours. The hot solution was decanted from the residue, and on cooling the acid crystallised out. The tarry residue was

repeatedly extracted with the mother liquor, hydrochloric acid (10 ml.) being added each time to facilitate hydrolysis. A total yield of 7·5 g. of the acid was obtained. It crystallised from a mixture of benzene and light petrol in needles, m.p. 108–09°. $\lambda_{max} = 255$ mμ ($\epsilon = 12{,}200$) (see Curve I of Figure). (Found: C, 70·1, H, 6·7. Theory: C, 70·1, H, 6·6.)

9-*Methyl*-3, 3 *a*, 4, 5-*tetrahydro*-6, 7-*benzindenone*-2-*acetic acid*-1 (*III*).—The valeric acid (6 g.) was refluxed for an hour with pottasium hydroxide (8 g.) in water (400 ml.). The cooled solution was filtered and acidified with dilute sulphuric acid. The acid crystallised from the methanol. m.p. 198–99°. Yield 4 g. $\lambda_{max} = 285$ mμ ($\epsilon = 17{,}300$). (see Curve III of Figure). (Found: C, 74·14, H, 6·58. Theory: C, 74·42, H, 6·97.)

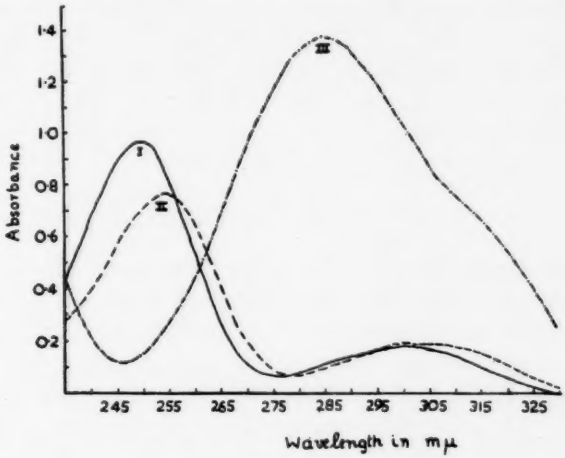


FIG. 1

2: 4-*Dinitrophenylhydrazone*.—The hydrazone separated as red fluffy mass when a freshly prepared hydrazine solution was added to the keto acid dissolved in ethanol. It crystallised from acetic acid, m.p. 259° (decomp.). (Found: C, 60·8, H, 4·9, N, 12·84. Theory: C, 60·5, H, 4·6, N, 12·84.)

9-*Methyl-tetrahydro*-6, 7-*benzindane-acetic acid*-1 (*IV*).—The above acid (4 g.) in absolute ethanol (60 ml.) containing concentrated sulphuric acid (3 ml.) was hydrogenated at 45 lb./sq. in., with 900 mg. previously reduced palladous oxide. Two molecules of hydrogen were taken up in two hours and the third molecule took a further nine hours. The solution was filtered from the catalyst, poured into water and extracted with ether. The etheral solution was washed successively with dilute potassium hydroxide and water.

The etheral solution contained the ester of the reduced acid, esterification having taken place during reduction. The ester obtained by the removal of the ether was saponified with N-methyl alcoholic potash and the acid liberated with dilute sulphuric acid. The product was isolated by ether extraction, yielding 3·5 g. of oily acid (IV), which could not be purified for analytical purposes. It was used in the next step without purification.

3-*Methyl*-4, 5, 6, 6 *a-tetrahydro*-6, 7-*aceperinaphthanone*-4 (*V*).—The above oily acid (3·5 g.) was dissolved in thiophene-free benzene (20 ml.) and treated with phosphorous pentachloride (7 g.). After an hour a solution of stannic chloride (5 ml.) in benzene (20 ml.) was added with ice cooling and shaking. The reaction mixture was maintained at 0° for two hours, then poured into ice-water, decomposed with hydrochloric acid and extracted with ether. The soluition was washed with dilute potassium hydroxide and water and dried over magnesium sulphate. The recovered product (2·5 g.) crystallised from methanol in colourless needles, m.p. 80°. Semicarbazone, m.p. 207° (decomposition). $\lambda_{max} = 255\ m\mu$ ($\epsilon = 9{,}560$) (see Curve II, in Figure). (Found: C, 84·53, H, 7·99. Theory: C, 84·96, H, 7·96.)

ACKNOWLEDGEMENT

My thanks are due to Dr. K. N. Menon for his valuable guidance, and to Government of Madras, for a Scholarship. I thank Mr. Selvavinayagam for analysis and Dr. Ramaswamy for U.V. data.

SUMMARY

The synthesis of 3-methyl-4, 5, 6, 6 *a*-tetrahydro-6, 7-aceperinaphthanone-4 is reported.

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COMPLEX COMPOUNDS OF THORIUM OXALATE WITH AMMONIUM OXALATE

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Received March 7, 1958

(Communicated by Dr. M. R. A. Rao, F.A.SC.)

Abstract

The system thorium oxalate-ammonium oxalate-water has been investigated by physico-chemical methods. A new procedure is adopted in preparing the solution for these studies by the mono-variation method. Data have been presented to prove the existence of two complexes in solution from measurements of electrical resistance, pH and relative viscosity.

Solubility of thorium oxalate in ammonium oxalate solution is the basis for one of the separatory methods of thorium from rare-earths.[1] The separation is not very specific or complete as some of the rare-earth oxalates are also dissolved to some extent. Brauner[2] describes two series of double salts with thorium oxalate and ammonium oxalate in the molar ratios of 1 : 1 and 1 : 2. No details of the method of preparation are given except that they can be crystallised from a concentrated solution of thorium oxalate in ammonium oxalate solution. Wyrouboff and Verneuil[3] assign a general formula $M_4(Th\,OX_4)\,NH_2O$ for the complexes, where M stands for K, Na or NH_4. However the methods adopted for the preparation or analysis are not available. No systematic attempt seems to have been made as yet, to ascertain the exact number and nature of the complexes formed between thorium oxalate and ammonium oxalate.

The system thorium oxalate-ammonium oxalate-water is investigated by studying some physico-chemical properties by the well-established procedures. For this type of study, two methods are available, *viz.*, the method of continuous variation originated by Job[4] and a modification of Job's method generally known as the method of mono-variation. Nair and Nair[5] have shown that the method of mono-variation is more suitable for the studies under reference. The insolubility of thorium oxalate in water creates an unusual problem in adopting the usual procedure for this type of studies. Use of a soluble salt of thorium, say, the nitrate would introduce the nitrate

ion in the system whose presence might influence the properties studied and make interpretation of results difficult. To avoid the uncertainty in these respects by the introduction of a different anion in the system, thorium oxalate itself is used and a new procedure is followed. No reference to the study of a similar system where one of the components is insoluble in the medium, is available. The procedure now adopted might find general application in studying similar systems by the method of mono-variation. But, reversal of the variant and constant for checking the results, as in the usual mono-variation method, may be practicable only within narrow limits of concentration.

EXPERIMENTAL

Materials used

Ammonium oxalate.—A.R. quality, recrystallised from conductivity water.

Thorium oxalate.—A.R. quality, B.D.H. make thorium nitrate was dissolved in water and precipitated with oxalic acid solution. The thorium oxalate was collected on the filter, washed free of oxalic acid with conductivity water, and dried in a current of air to get a product of constant composition $Th(C_2O_4)_2\,6\,H_2O$.

Water.—Double distilled water was again distilled in an all-silica distillation unit.

Preparation of solutions

After preliminary experiments on the solubility of thorium oxalate in ammonium oxalate solution, it was decided to use M/4 ammonium oxalate solution to which known weights of thorium oxalate were added and after dissolution made up to 100 ml.

(1) *Measurement of electrical resistance.*—The cell used had vertical electrodes, separated by a distance of 3·5 cm. The electrodes were freshly platinized and the cell was thoroughly cleaned before use. The cell was filled with the solution to the required level and kept in a thermostat maintained at $30° \pm 0·05°$ C. and the resistance measured by the null point method. Results are given in Table I and represented in Fig. 1.

(2) *pH measurements.*—A Beckman pH meter model H-2 was used to measure the pH of the solutions. The electrodes were washed several times with distilled water and then with the respective solution before each measurement. The results are given in Table I and represented in Fig. 2.

TABLE I

Electrical resistance, pH and relative viscosity at 30° ± 0·05° C. of the system $Th\ (C_2O_4)_2$—$(NH_4)_2\ C_2O_4$—H_2O

Soln. No.	Strength of the solution in molarity with respect to: Ammonium Oxalate	Thorium Oxalate	Electrical resistance (Ohms)	pH	Relative viscosity
1	0·1	0·01000	58·20	7·18	1·1666
2	,,	0·01125	60·20	6·75	1·1676
3	,,	0·01250	59·45	7·00	1·1220
4	,,	0·01375	60·24	6·70	1·1461
5	,,	0·01625	61·40	6·92	1·1700
6	,,	0·01875	63·20	6·90	1·1720
7	,,	0·02375	65·20	6·80	1·1717
8	,,	0·02500	67·70	6·98	1·1491
9	,,	0·02625	65·80	6·40	1·1604
10	,,	0·02875	66·30	6·15	1·1834

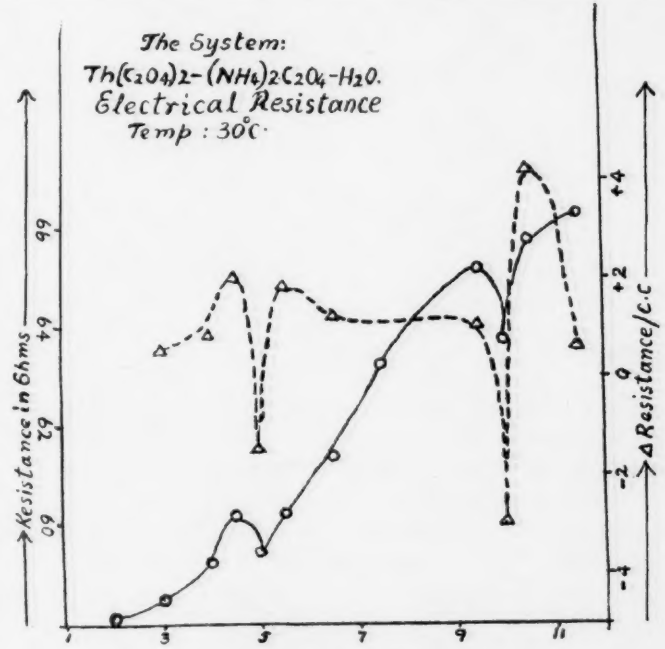
The System:
Th(C2O4)2-(NH4)2C2O4-H2O.
Electrical Resistance
Temp : 30°C.
Resistance in Ohms
Δ Resistance/c.c
No. of c.c. [eq. to the wt. added] of M/4 Th. Oxal
added to 40 c.c. of M/4 Am. Oxal. Soln. and
made up to 100 c.c.

FIG. 1

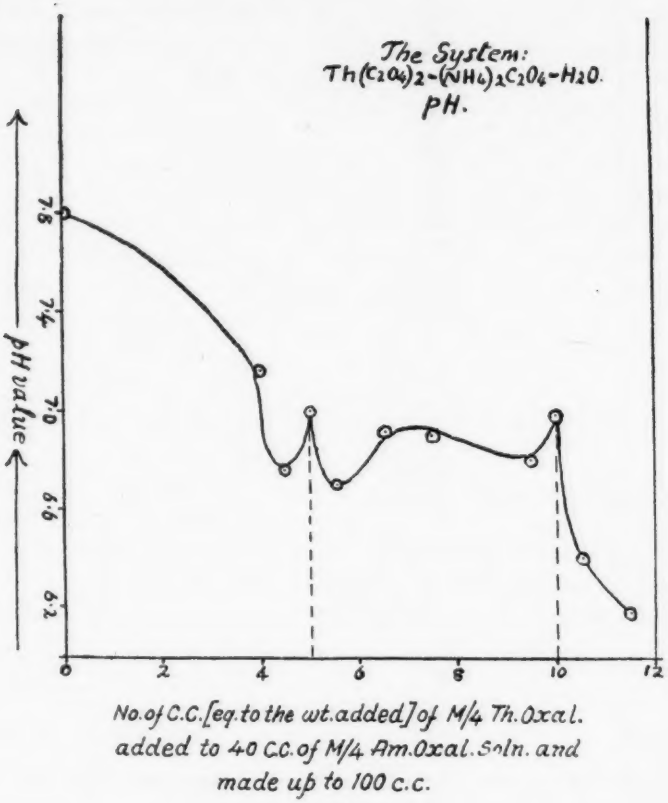

FIG. 2

(3) *Density and viscosity measurements.*—An Ostwald viscometer was used to measure the viscosity. The flow rate for distilled water was 640 seconds for the instruments, and the capacity of the bulb was 25 ml. All the measurements were made with the viscometer clamped vertically in a thermostat maintained at $30° \pm 0{\cdot}05°$ C. Readings were taken for distilled water and for the ten solutions. The densities of these solutions were measured at the same temperature using a Pyknometer. Data are presented in Table I and represented graphically in Fig. 3.

(4) *Attempts to isolate the complexes.*—Solutions 3 and 8 were taken in separate crystallising dishes and slowly evaporated on the water-bath. The solid separated in both cases was found to be a mixture of the thorium oxalate and ammonium oxalate. Evaporation of the solutions under vacuum or in

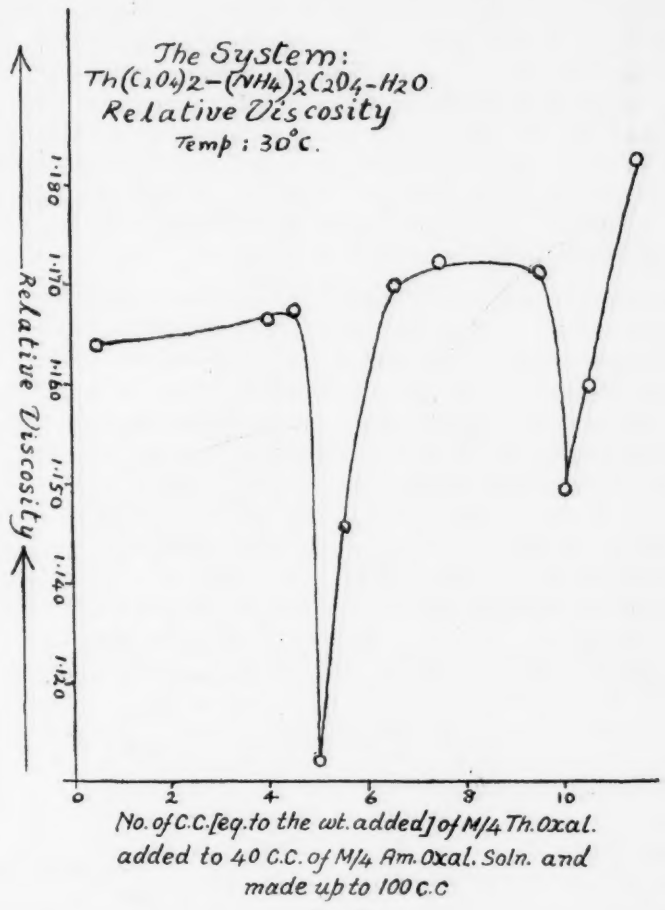

FIG. 3

a desiccator did not yield the pure crystals. Even from solutions of higher concentration, the complexes could not be isolated in the solid state.

DISCUSSION

Although it has not been possible to isolate the complex of thorium oxalate and ammonium oxalate, sufficient data have been collected to prove the existence of two complexes in solution. In all the three properties investigated some abnormality is noticed in the values at two points where the molar ratios of thorium oxalate to ammonium oxalate is 1 : 8 and 1 : 4,

The appearance of these abnormalities in the graphs obtained by plotting the values of these diverse properties against the volume of M/4 thorium oxalate added, is convincing proof of the existence of two complexes in solution. Since 40 ml. of M/4 ammonium oxalate is present in each solution, it is evident that the two points corresponding to 5 ml. and 10 ml. of thorium oxalate, represent the formation of compounds between the two salts in the molar ratios 5:40 and 10:40 or 1:8 and 1:4. Accordingly the two complexes may be represented as $Th(C_2O_4)_2$—8 $(NH_4)_2 C_2O_4$ and $Th(C_2O_4)_2$—4 $(NH_4)_2 C_2O_4$.

The maximum amount of thorium oxalate added is 1·4198 gm. corresponding to 11·5 ml. of M/4 solution. Larger quantities than this amount of thorium oxalate cannot be added as the solubility limits in 40 ml. of M/4 ammonium oxalate solution will have exceeded. Therefore, solutions corresponding to 1:1 or 1:2 molar ratios of the two salts cannot be prepared and investigated in the manner described earlier. It is not suggested by any means, that a complex containing the two salts in the ratio 1:1 or 1:2 will be formed only from a mixture of the two solutions having the salts in the above ratios. All the attempts by the present authors to obtain the complexes described by the early workers have failed. However, the present studies have very definitely proved the existence of two complexes in solution.

The authors are grateful to Dr. P. P. Pillay, Professor of Applied Chemistry, University of Kerala, for his keen interest in the work.

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POLAROGRAPHIC BEHAVIOUR OF ORGANIC IODOCOMPOUNDS

Part I. Iodobenzene

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Received April 23, 1958

(Communicated by Prof. K. R. Krishnaswami, F.A.SC.)

Introduction

It has been noticed[1-7] that the presence of an organic solvent in the base solutions has a profound influence on the polarographic characteristics of substances. This phenomenon assumes special significance in the polarographic studies of organic substances, since in the case of these substances a base solution containing an aqueous mixture of an organic solvent is commonly employed. The present work deals with the study of the influence of organic solvents, namely, ethanol, dioxane and acetone, on the polarographic behaviour of comparatively simple substances such as iodobenzene, iodonaphthalene and *o*-, *m*- and *p*-iodobenzoic acids. The diffusion coefficients of these substances under polarographic conditions have been determined by the diaphragm cell technique, since the diffusion coefficient is one of the major factors influencing the diffusion current constant. In this communication the results relating to iodobenzene have been presented.

Experimental

The essential experimental techniques for recording and measuring the polarograms have been the same as described previously.[8] To prevent the evaporation of the solvent or the organic compound, hydrogen is initially equilibrated with the test solutions. The value of 'm' for the dropping mercury electrode employed has been 1·431 mg. per second and the droptime 't' has been adjusted to be 5 seconds in normal potassium chloride solution. The polarograms have been taken at $30° \pm 0·1°$ C.

Iodobenzene[9, 10] is prepared from aniline through benzene diazonium chloride. Ethanol, dioxane and acetone have been purified by standard methods.[11, 12] Pure lithium chloride is prepared from reprecipitated lithium

carbonate. In solutions where maxima appear gelatin is used as the maximum suppressor.

Measurement of the diffusion coefficient of iodobenzene

1. *Diaphragm cell method.*—The diaphragm cell technique has been standardised for the measurement of the diffusion coefficients under polarographic conditions. The symmetrical double-ended cell described by Mc Bain and Dawson[13] is employed in the present work. Both the upper and lower compartments are fitted with 2 stop-cocks each, so that either compartment can be emptied or filled without disturbing the liquid in the other compartment or the diaphragm. The diaphragm is made up of pyrex sintered glass of medium porosity (10–15 μ). The volumes of the upper and lower compartments are 35·30 and 36·64 c.c. respectively.

While measuring the diffusion coefficient of iodobenzene, the upper compartment is filled with the test solution containing iodobenzene (3–15 millimolar) in the suitable base solution (without gelatin) while the lower compartment contains only the base solution. After allowing the diffusion column to be set up within the diaphragm both the compartments are emptied and refilled with their respective base solutions. The experiments are conducted in an air thermostat kept at 30° ± 0·1° C. A period of 16–144 hours is needed to allow enough of iodobenzene to diffuse into the lower compartment, depending upon the concentration of iodobenzene in the upper compartment, to allow polarographic estimation. The diffusion coefficients are then calculated using the King and Cathcart[14] equation

$$\beta D t = \frac{V_A V_B}{V_A + V_B} \log \left[\frac{C_0}{C_0 - \left(1 + \frac{V_B}{V_A}\right) C} \right]$$

where β = the cell constant, D = the diffusion coefficient of the substance (cm.^{2} per second), t = the duration of the diffusion experiment in seconds, V_A = the volume of the upper compartment, V_B = the volume of the lower compartment, C_0 = the initial concentration of the diffusing substance in the upper compartment, and C = the final concentration of the diffused substance in the lower compartment at the completion of the experiment.

The cell constant β is determined using potassium chloride as the reference substance. The average value of β is 0·5872 log units per second.

The diffusion coefficients for iodobenzene have been measured employing different concentrations of the three organic solvents namely, alcohol, dioxane and acetone. Each value is the average of five independent determinations. The values have been found to be reproducible within ± 1%.

The results are presented in Table I. It is clear from the table that the diffusion coefficient of iodobenzene is different in the three solvents employed. Further, there is a marked increase in the values of the diffusion coefficients when the concentration of the organic solvent is increased.

TABLE I

Effect of concentration of organic solvent on the diffusion coefficient of iodobenzene by diaphragm cell method

Ethanol		Dioxane		Acetone	
% by volume	$D \times 10^6$ sq.cm./sec.	% by volume	$D \times 10^6$ sq.cm./sec.	% by volume	$D \times 10^6$ sq.cm./sec.
10	0·377	10	1·83	10	1·30
25	1·32	25	3·56	20	3·42
50	3·93	40	4·11	25	5·15
75	6·36	50	4·39	50	7·48
98	12·10	60	4·42	60	9·54

2. *Viscosity method.*—The viscosities of the base solutions have been determined at 30° ± 0·05° C., employing the Ostwald viscometer, using benzene and water as reference substances. The diffusion coefficient has been calculated by Stokes-Einstein diffusion equation[15] which has been modified to suit the polarographic conditions.

$$D = \frac{3 \cdot 009 \times 10^{-7}}{\eta (V_m)^{\frac{1}{3}}} \text{ at } 30° \text{ C.},$$

where η = viscosity of the medium and V_m = the apparent molar volume.

Taking a value of 130·5[16] for the molar volume of iodobenzene, the diffusion coefficients have been calculated employing the experimentally determined values of η of the base solutions used and the results of such calculations are given in Table II. It is clear from this table that the diffusion coefficients decrease with an increase in the concentrations of the organic solvents used while the reverse is true when the diffusion coefficients are measured directly by the diaphragm cell method. To facilitate comparison the diffusion coefficients measured by the cell technique and those derived from viscosity data are placed alongside in Table III.

3. *Equivalent conductivity data.*—The diffusion coefficient of iodobenzene can be derived from equivalent conductivity at infinite dilution of *o*-iodobenzoic acid.[17, 18] Equivalent conductivity data has given a value of

TABLE II

Diffusion coefficient of iodobenzene at different concentrations of organic solvent computed from viscosity data

Concentration of lithium chloride=1M.

Ethanol			Dioxane			Acetone		
% by volume	η of the base solution (centi-poises)	$D \times 10^6$ sq.cm./ sec.	% by volume	η of the base solution (centi-poises)	$D \times 10^6$ sq.cm./ sec.	% by volume	η of the base solution (centi-poises)	$D \times 10^6$ sq.cm./ sec.
10	1·184	5·01	10	1·150	5·17	10	1·093	5·43
25	1·650	3·60	25	1·559	3·81	20	1·263	4·70
50	2·318	2·56	40	2·079	2·85	25	1·371	4·33
75	2·653	2·24	50	2·444	2·43	50	1·445	4·11
98	2·820	2·10	60	2·638	2·25	60	1·445	4·11

TABLE III

Diffusion coefficient of iodobenzene at different concentrations of the organic solvent by diaphragm cell (D) *and viscosity* (V)

Solvent	Diffusion coefficient $\times 10^6$ (sq. cm./sec.) in various concentrations (% by volume) of organic solvent													
	10		20		25		40		50		60		75		98	
	D	V	D	V	D	V	D	V	D	V	D	V	D	V	D	V
Ethanol..	0·377	5·01	..		1·32	3·60	..		3·93	2·56	..		6·36	2·24	12·10	2·10
Dioxane..	1·83	5·17	..		3·56	3·81	4·11	2·85	4·39	2·43	4·42	2·25	..		..	
Acetone..	1·30	5·43	3·42	4·70	5·15	4·33	..		7·48	4·11	9·54	4·11	..		..	

$8{\cdot}54\times10^{-6}$ sq. cm. per sec. for the diffusion coefficient of iodobenzene acid at 25° C. The calculated value for the diffusion coefficient of iodobenzene is $9{\cdot}40\times10^{-6}$ sq.cm. per sec. at 25° C. Taking the temperature coefficient of the diffusion coefficient as 2%,[19] the diffusion coefficient of iodobenzene at 30° C. is calculated as $10{\cdot}34\times10^{-6}$ sq.cm. per sec. It is obvious that equivalent conductivity data leads to only one value of the diffusion coefficient while the diaphragm cell and viscosity methods give different values of the diffusion coefficient at various concentrations of the organic solvent. Further, it has been found that the diffusion coefficients obtained by the diaphragm cell and viscosity methods depend also on the organic solvent employed.

Measurement of polarographic characteristics of iodobenzene

Preliminary experiments in aqueous media containing 50% ethanol and different concentrations of lithium chloride indicated that, when the concentration of lithium chloride is one molar, well-defined polarographic waves are obtained. With an increase in the concentration of lithium chloride above one molar, a decrease in the diffusion current constant is noticed. The diffusion current constant is 2·39 and 1·42 when the concentration of lithium chloride is 1 M and 2 M respectively. Consequently 1 M lithium chloride has been employed as the indifferent electrolyte.

1. *Effect of concentration of ethanol, dioxane and acetone on the diffusion current constant, half-wave potential, $E_{\frac{3}{4}}$–$E_{\frac{1}{4}}$ and wave forms of iodobenzene.*—Some of the polarograms showing the effect of the concentration of ethanol and dioxane on the polarographic waves of iodobenzene are given in Figs. 1, 2, 3, 4 and 5. The appearance of the waves in acetone have been found to be similar to those obtained in ethanol. It has to be pointed out, however, that the wave forms are best in dioxane. Solutions containing more than 60% dioxane or acetone have not been used due to the high resistance of the circuit. The results of analysis of the waves are presented in Table IV.

Examination of the results presented in Table IV indicates that an increase in the concentration of the organic solvent brings about an increase in the diffusion current constant. This is surprising since this behaviour is entirely different from that noticed in the case of other organic and inorganic substances. The half-wave potential becomes more negative with an increase in the solvent concentration. The values of $E_{\frac{3}{4}}$–$E_{\frac{1}{4}}$ are of the order of 0·09 V indicating that the reduction process is irreversible in nature.

2. *Effect of concentration of iodobenzene on the diffusion current constant, half-wave potential and $E_{\frac{3}{4}}$–$E_{\frac{1}{4}}$.*—Analysis of the polarograms obtained at

TABLE IV

Effect of the concentration of organic solvent on the polarographic behaviour of iodobenzene

Organic solvent	% by volume of organic solvent	Diffusion current constant	$E_{\frac{1}{4}}$ *vs.* S.C.E. (volt)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (volt)
Ethanol ..	10	0·72	−1·583	0·089
..	25	1·31	−1·652	0·091
..	50	2·39	−1·681	0·091
..	75	2·95	−1·726	0·095
..	98	3·77	−1·805	0·097
Dioxane ..	10	1·52	−1·581	0·102
..	25	2·23	−1·642	0·103
..	40	2·33	−1·656	0·100
..	50	2·39	−1·700	0·105
..	60	2·43	−1·715	0·108
Acetone ..	10	1·34	−1·587	0·097
..	20	2·21	−1·595	0·098
..	25	2·59	−1·597	0·102
..	50	3·21	−1·650	0·105
..	60	3·46	−1·660	0·102

different concentrations of iodobenzene, in presence of various concentrations of dioxane, alcohol and acetone indicates that the half-wave potential becomes slightly more positive when the concentration of iodobenzene is increased. For example, it has been found that in 50% ethanol, the half-wave potential shifts from − 1·690 V to − 1·621 V (*vs.* S.C.E.) when the concentration of iodobenzene is changed from 0·3 millimoles per litre to 20 millimoles per litre. The value of $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ remains more or less at 0·09 V. In Table V are presented the results showing the effect of concentration of iodobenzene on the diffusion current constant in presence of different amounts of the organic solvent. It has to be pointed out that, when the concentration of alcohol or dioxane in the base solution is 50% and above, maximum appears at higher concentrations of iodobenzene (>6 millimolar). To eliminate this maximum 0·001–0·002% gelatin is used. In dioxane solutions the hump is not completely eliminated. This complexity, however, does not affect the proportionality of the diffusion current with the concentration of iodobenzene. Some

TABLE V

*Effect of the concentration of iodobenzene on the diffusion current constant in aqueous mixtures ethanol, dioxane and acetone**

Concentration of lithium chloride = 1 M.

Concentration of iodobenzene (Millimolar)	Diffusion current constant I	Concentration of iodobenzene (Millimolar)	Diffusion current constant I	Concentration of iodobenzene (Millimolar)	Diffusion current constant I
(1)		(5)		(9)	
25% ethanol		25% dioxane		10% acetone	
X=1·580 at −1·87 V *vs.* S.C.E.		X=1·550 at −1·87 V *vs.* S.C.E.		X=1·545 at −1·87 V *vs.* S.C.E.	
0·390	1·31	0·441	2·29	0·390	1·34
0·780	1·31	0·571	2·27	0·780	1·34
3·120	1·30	1·712	2·23	1·561	1·34
4·680	1·31	2·188	2·22		
		4·376	2·23		
(2)		(6)		(10)	
50% ethanol		40% dioxane		20% acetone	
X=1·522 at − 1·87 V *vs.* S.C.E.		X=1·540 at −1·87 V *vs.* S.C.E.		X = 1·550 at −1·87 V *vs.* S.C.E.	
0·313	2·37	0·571	2·33	0·390	2·24
0·730	2·40	1·141	2·33	0·780	2·21
2·128	2·40	2·282	2·35	1·561	2·21
6·043	2·33	4·564	2·33	3·122	2·21
10·00	2·33	9·128	2·32	6·244	2·21
20·00	2·35				
(3)		(7)		(11)	
75% ethanol		50% dioxane		50% acetone	
X=1·529 at −1·92 V *vs.* S.C.E.		X=1·554 at −1·95 V *vs.* S.C.E.		X=1·541 at −1·95 V *vs.* S.C.E.	
0·313	2·99	0·582	2·39	0·780	3·20
2·128	2·95	1·164	2·39	1·561	3·22
6·384	2·93	2·328	2·38	5·430	3·19
10·00	2·85	6·985	2·37	6·500	3·02
20·00	2·83	10·00	2·34	10·00	3·03
(4)		(8)		(12)	
98% ethanol		60% dioxane		60% acetone	
X=1·528 at −1·97 V *vs.* S.C.E.		X=1·545 at −1·97 V *vs.* S.C.E.		X=1·549 at −1·95 V *vs.* S.C.E.	
0·730	3·78	0·668	2·43	0·780	3·45
2·128	3·76	1·336	2·43	1·561	3·46
3·192	3·77	2·673	2·36	3·122	3·45
5·00	3·76	5·346	2·37	5·430	3·43
10·00	3·76	8·018	2·38	7·502	3·43
				10·00	3·43

* Abbreviation :—X—$m^{2/3}\,t^{1/6}$ in $mg.^{2/3}\,sec.^{-1/2}$.

experiments have been performed incorporating a small amount of gelatin (0·001%) even when no maximum appears on the C-V Curve. It has been found that this does not have any noticeable effect either on the diffusion current or on the half-wave potential.

Calculation of the number of electrons involved in the reduction process from the Ilkovic Equation.—Lingane[20] has defined the term diffusion current constant (I) by a rearrangement of the Ilkovic equation

$$I = 607n\,D^{\frac{1}{2}} = \frac{i_d}{Cm^{\frac{2}{3}}t}$$

where i_d = the average diffusion current in microamperes during the life of a drop, C = concentration of the electroreducible substance in millimoles per litre, m, t, n and D have the usual significance. Employing the experimentally determined values of the diffusion current constants and the diffusion coefficients obtained by the diaphragm cell, viscosity and equivalent conductivity methods outlined above, the number of electrons involved in the reduction process has been calculated and the values are given in Table VI.

DISCUSSION

1. *Relationship between the diffusion coefficient and the diffusion current constant of iodobenzene and the mechanism of the reduction process of iodobenzene.*—It has to be pointed out that very little work has been done on the effect of the concentration of the organic solvent either on the diffusion coefficient or on the polarographic behaviour of substances, particularly the organic compounds. It has been the common practice, in polarographic work, to incorporate arbitrarily chosen concentrations of organic solvents in the aqueous base solutions to render the substance soluble. It is noteworthy that the diffusion current constant (Table IV) of iodobenzene increases with an increase in the concentration of the organic solvent, contrary to the observations of previous workers with other organic compounds. For example, the diffusion currents determined by Kolthoff and Lehmicke[3] for phenolphthalein and benzoquinone show a decrease with an increase in the concentration of ethanol. Similar decrease with rise in ethanol concentration has also been noticed for potassium, sodium and lithium ions by Peracchio and Meloche.[1] It is surprising that in the case of iodobenzene, an increase in the concentration of the organic solvent should have enhanced the value of the diffusion current constant. Such an anomalous behaviour has not been noticed by previous workers.

It is, however, significant that the diffusion coefficient determined by the diaphragm cell method (Table I) also increases with an increase in the

TABLE VI

Number of electrons involved in the reduction of iodobenzene in aqueous mixtures of ethanol, dioxane and acetone calculated employing the diffusion coefficients from the diaphragm cell, conductivity and viscosity methods

Concentration of lithium chloride = 1 M.

Organic solvent	% by volume of organic solvent	'*n*' calculated from the diffusion coefficient		
		1 by diaphragm cell method	2 conductivity method	3 viscosity method
Ethanol ..	10	1·9	0·4	0·5
..	25	1·9	0·7	1·1
..	50	2·0	1·2	2·5
..	75	1·9	1·4	3·0
..	98	1·8	1·9	4·3
Dioxane ..	10	1·8	0·8	1·1
..	25	1·9	1·1	1·9
..	40	1·9	1·2	2·3
..	50	1·9	1·2	2·5
..	60	1·9	1·2	2·7
Acetone ..	10	1·9	0·7	0·9
..	20	2·0	1·1	1·7
..	25	1·9	1·3	2·1
..	50	1·9	1·6	2·6
..	60	1·8	1·8	2·8

concentration of the organic solvent. On graphical analysis, it has been found that the diffusion current constants are related to these diffusion coefficients by the parabolic law $I \propto D^{\frac{1}{2}}$. This conclusion is in agreement with the theoretical Ilkovic equation. On the other hand, the diffusion coefficients deduced from viscosity data decrease with an increase in the concentration of the organic solvent. Combination of the Ilkovic equation with the Stokes-Einstein equation leads to the relationship $I\sqrt{\eta} = \text{constant}$. It has been found that in the case of iodobenzene $I\sqrt{\eta}$ is not a constant. The number of electrons involved in the reduction process (Table VI) is nearly two when the diffusion coefficients determined by the diaphragm cell are used, while when the diffusion coefficients calculated from viscosity data are employed, the values of '*n*' vary from 0·5 to 4·3. This clearly indicates that Stokes-Einstein equation has limitations and the diffusion coefficients obtained from this

equation have limited applicability for evaluating the reduction mechanism. Equivalent conductivity data lead to only one value of the diffusion coefficient and are obviously inadequate to explain the large variations in the value of the diffusion current constant that have been observed in the case of iodobenzene. The values of 'n' calculated on this basis vary between 0·4 to 1·9. It is therefore clear that it is desirable to determine the diffusion coefficients under polarographic conditions and to employ these values in the Ilkovic equation for determining the mechanism of the reduction process. It is obvious that the changes in the diffusion coefficient determined experimentally are not merely due to changes in the viscosity of the solution. Other factors such as solvation play a very important role.

The following reduction mechanism can therefore be suggested for iodobenzene at all concentrations of the three organic solvents employed in the present work.

$$C_6H_5I + 2\,e + H^+ \rightarrow C_6H_6 + I^-$$

This agrees with the reduction mechanism proposed by Stackelberg and Stracke[21] for iodobenzene in 75% dioxane. Gergely and Iredale[18] have confirmed the above mechanism by large-scale electrolysis. The present work further shows that the reduction mechanism is unaffected by the nature of the solvent or its concentration. It has to be pointed out that Runner and Wagner[22] and Runner[23] have studied the reduction of nitroacetanilide and nitroaniline in buffered solutions of ethanol and also determined the diffusion coefficient under polarographic conditions in order to ascertain independently the reduction mechanism.

2. *Effect of concentration of the organic solvent on the half-wave potential and* $E_{\frac{3}{4}}$–$E_{\frac{1}{4}}$.—In all three solvents it has been noticed (Table IV) that with an increase in the concentration of the organic solvent, the half-wave potential shifts to more negative values indicating greater difficulty in the reduction of iodobenzene. The values of $E_{\frac{3}{4}}$–$E_{\frac{1}{4}}$ (Table IV) are of the order of 0·09 V indicating that the reduction process is irreversible in character.

SUMMARY

1. The diffusion coefficients and the diffusion current constants of iodobenzene have been determined in aqueous mixtures of ethanol, dioxane and acetone containing 1 M lithium chloride. The diffusion current constant is found to be proportional to the square-root of the diffusion coefficient determined by the diaphragm cell technique and the number of electrons involved in the reduction process is found to be two. The diffusion coefficients determined by the viscosity and conductivity methods do not explain

the anomalous variation of the diffusion current constant with solvent concentration noticed in the case of iodobenzene and they lead to erroneous conclusions regarding the reduction mechanism.

2. It has been found that half-wave potential shifts to more negative values with an increase in the concentration of the organic solvent. The values of $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ have been found to be of the order of 0·09 V in all media indicating the irreversibility of the electrode process. It has been suggested that the polarographic method can be used for the estimation of iodobenzene.

ACKNOWLEDGEMENT

The authors wish to express their sincere thanks to Prof. K. R. Krishnaswami and Prof. M. R. A. Rao for their helpful discussions.

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592-58. Printed at The Bangalore Press, Bangalore City, by C. Vasudeva Rao, Superintendent, and Published by The Indian Academy of Sciences, Bangalore.

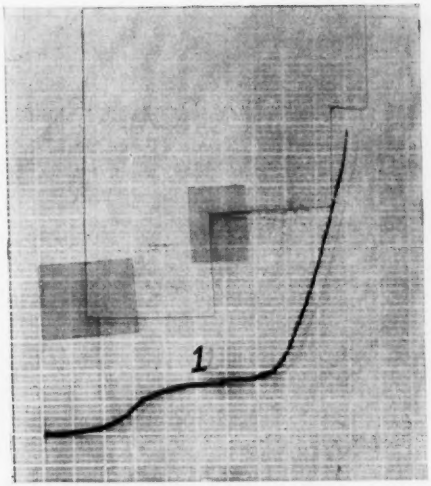

FIG. 1. Polarogram of iodobenzene ($0 \cdot 6925 \times 10^{-3}$ M) in 10% ethanol and 1·0 M lithium chloride.

Sensitivity: S/20.

The voltage line just before the beginning of the polarogram corresponds to $-1 \cdot 273$ V. *vs.* S.C.E.

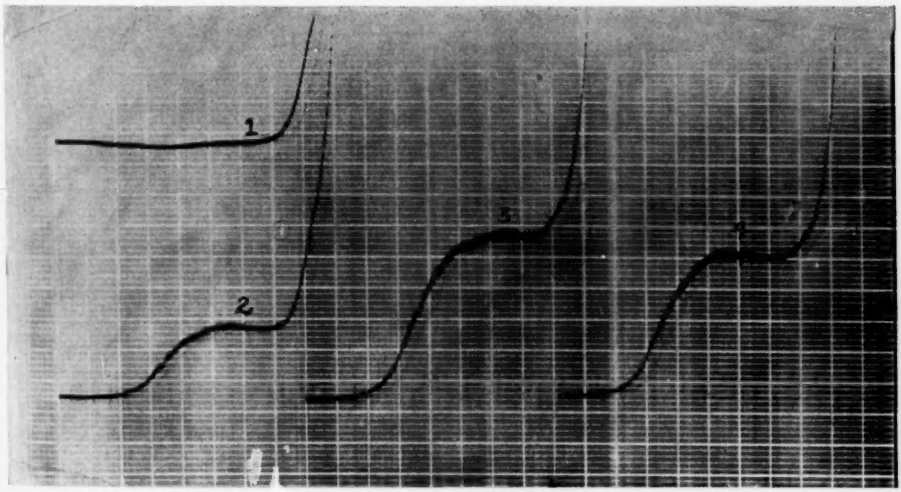

FIG. 2. Polarograms of iodobenzene in 25% ethanol and 1·0 M lithium chloride.

Curve 1 is blank at S/50; curves 2 to 4 are obtained with $0 \cdot 6766 \times 10^{-3}$ M, $1 \cdot 445 \times 10^{-3}$ M and $1 \cdot 415 \times 10^{-3}$ M iodobenzene, the sensitivity being S/50 in all the cases.

The voltage line preceding each polarogram corresponds to $-1 \cdot 273$ V. *vs.* S.C.E.

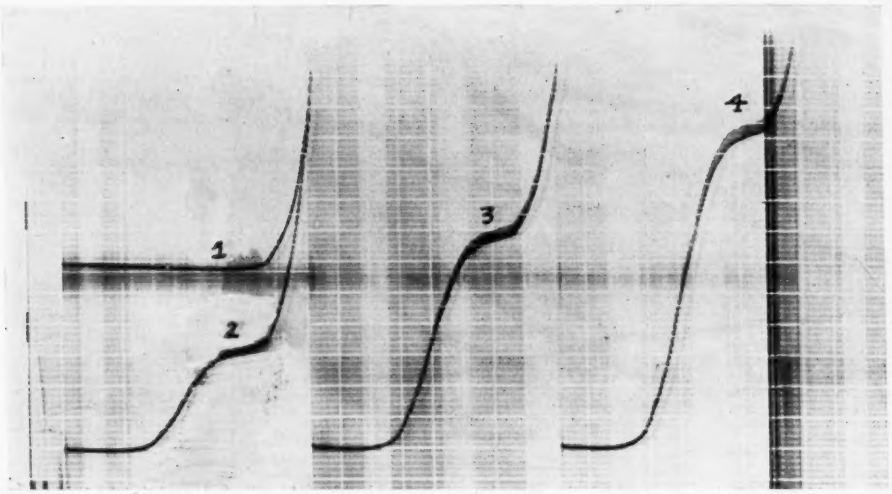

FIG. 3. Polarograms of iodobenzene in 50% ethanol and 1·0 M lithium chloride. Sensitivity: S/70; Concentration of gelatin 0·001%.

Curve 1 is blank; curves 2 to 4 have been taken with $1{\cdot}064\times10^{-3}$ M, $2{\cdot}128\times10^{-3}$ M and $3{\cdot}192\times10^{-3}$ M iodobenzene respectively.

The voltage line preceding each polarogram corresponds to $-1{\cdot}273$ V. *vs.* S.C.E.

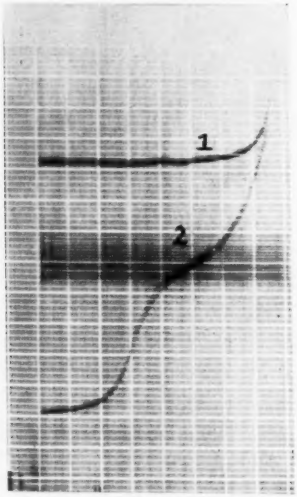

FIG. 4. Polarogram of iodobenzene in 10% dioxane and 1·0 M lithium chloride.

Sensitivity: S/20.

Curve 1 is blank; curve 2 has been taken with $0{\cdot}6925\times10^{-3}$ M iodobenzene.

The voltage line preceding each polarogram corresponds to $-1{\cdot}273$ V. *vs.* S.C.E.

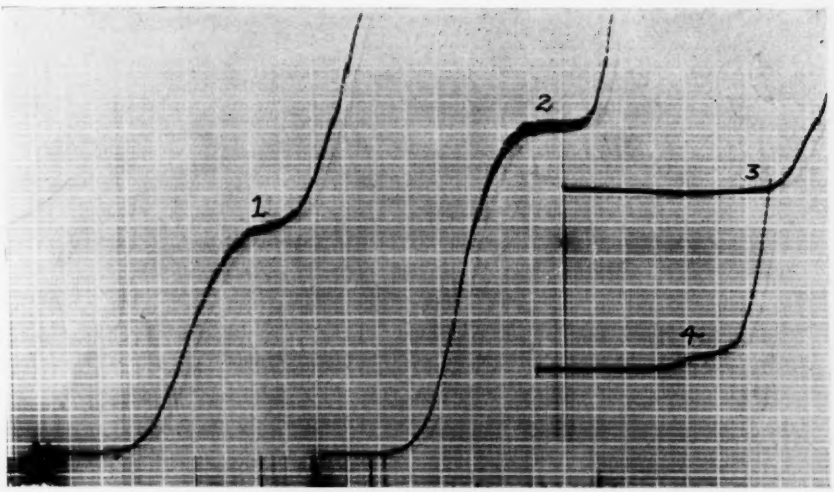

FIG. 5. Polarograms of iodobenzene in 50% dioxane and 1·0 M lithium chloride.
Curves 1 and 2 have been taken at sensitivity S/150 with $4{\cdot}944\times10^{-3}$ M and $7{\cdot}416\times10^{-3}$ iodobenzene respectively; Curves 3 and 4 are blanks at S/150 and S/100 respectively.
The voltage line preceding each polarogram corresponds to $-1{\cdot}273$ V. *vs.* S.C.E.

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